SOLAR ENERGY

THE JOURNAL OF SOLAR ENERGY SCIENCE AND ENGINEERING

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Photolysis of Nitrosyl Chloride in the Solar Furnace

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The use of the solar furnace as a cool, intense light source has recently been reported. This light source now has been used to initiate the photodissociation of nitrosyl chloride, a reaction proposed by Daniels for the photochemical storage of solar energy. Experiments are reported with three types of light-absorber systems: static, open, and flow systems. The conclusion reached was that fast flow systems will be necessary in order to avoid the back-reaction of the photoproducts.

The sun's energy may be stored by thermal, electrical, or chemical means. Chemical methods of solar energy storage require conversion of light energy to chemical potential energy. This conversion occurs when the free energy of formation of chemical compounds is supplied by light. The usual postulate for utilization of such processes is a photochemical reaction whose products are easily separated and can be recombined upon demand.[12]

We have completed one study on the use of the solar furnace as a light source. The reaction studied involved insolation of ceric perchlorate,[9, 10, 11] and showed that the oxidation of water to form oxygen and the corresponding reduction of ceric to cerous ion did take place at a reasonable rate at the focus of a rear-silvered solar furnace. This reaction,

$$Ce^{+4} + \frac{1}{2} H_2O \xrightarrow[HClO_4]{h\nu} Ce^{+3} + H^+ + \frac{1}{4} O_2, \quad [1]$$
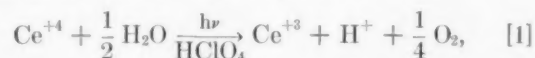
is of little use in the atmosphere for storage of the sun's energy without the concomitant formation of hydrogen which might occur in the photo-oxidation of cerous ion:

$$Ce^{+3} + H_2O \xrightarrow[HClO_4]{h\nu} Ce^{+4} + OH^- + \frac{1}{2} H_2. \quad [2]$$
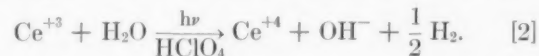
The evolution of hydrogen by this reaction has been reported in ultraviolet light[6] (2537 Å) and in sunlight.[5] Our experiments with cerous perchlorate showed that less than 2.5×10^{-6} moles of hydrogen (the limit of our analytical method) could have been formed at the focus of a front-silvered solar furnace in a 2-hour exposure. We are therefore looking for more promising systems for the storage of solar energy.

The photodecomposition of nitrosyl chloride is one possible system of utilizing solar energy. This reaction,

$$2 NOCl \xrightarrow{h\nu} 2 NO + Cl_2, \quad [3]$$
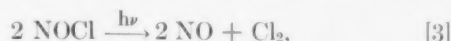
is listed in Daniels'[4] table of photochemical quantum yields. Thermodynamically the photodissociation of nitrosyl chloride is endergonic by 4.9 kcal/mole. The efficiency, Q, of conversion of radiant energy to chemical energy as defined by Calvert[3] is 21.8%. The free energy stored in the products of this reaction is available upon demand by recombination of the nitric oxide and chlorine to form the original nitrosyl chloride.

In order to prevent recombination of the product gases and concomitant waste of absorbed light, the reaction should take place in a solvent in which only one of the products is soluble. In this manner, the gases could be stored and later recombined to give the original nitrosyl chloride and to release the solar energy consumed in the decomposition.

EQUIPMENT AND OPERATING PROCEDURE

A two-foot solar furnace with front-silvered optics was used for the present study. Details of this furnace were described previously.[11]

Two different cells were designed and tested during the present study. The first cell was designed for a static system; a photograph of the cell at the focus of the solar furnace is shown in Fig. 1 and the construction details of the vessel as well as a flow diagram are shown in Fig. 2. This cell was made of Vycor glass, whose light transmission is about 70% in the 3000–3500 Å wavelength region in the geometry used here. Light rays entered the vessel from the paraboloid below and came to a focus inside the space enclosed by the cooling coils—about $1\frac{1}{4}$ in. above the bottom of the flask. No mechanical stirring was provided since sufficient mixing was obtained from gas bubbles rising to the surface.

The second type of cell was made from Pyrex glass for a gravity feed flow system. A photograph of one cell, and the construction details of both cells are shown in Fig. 3 and 4.

Prior to the start of an experiment, the system was thoroughly flushed with argon to displace atmospheric oxygen. Nitrosyl chloride, dissolved in carbon tetrachloride, was added to either system. During the equilibration period which followed, the coolant was
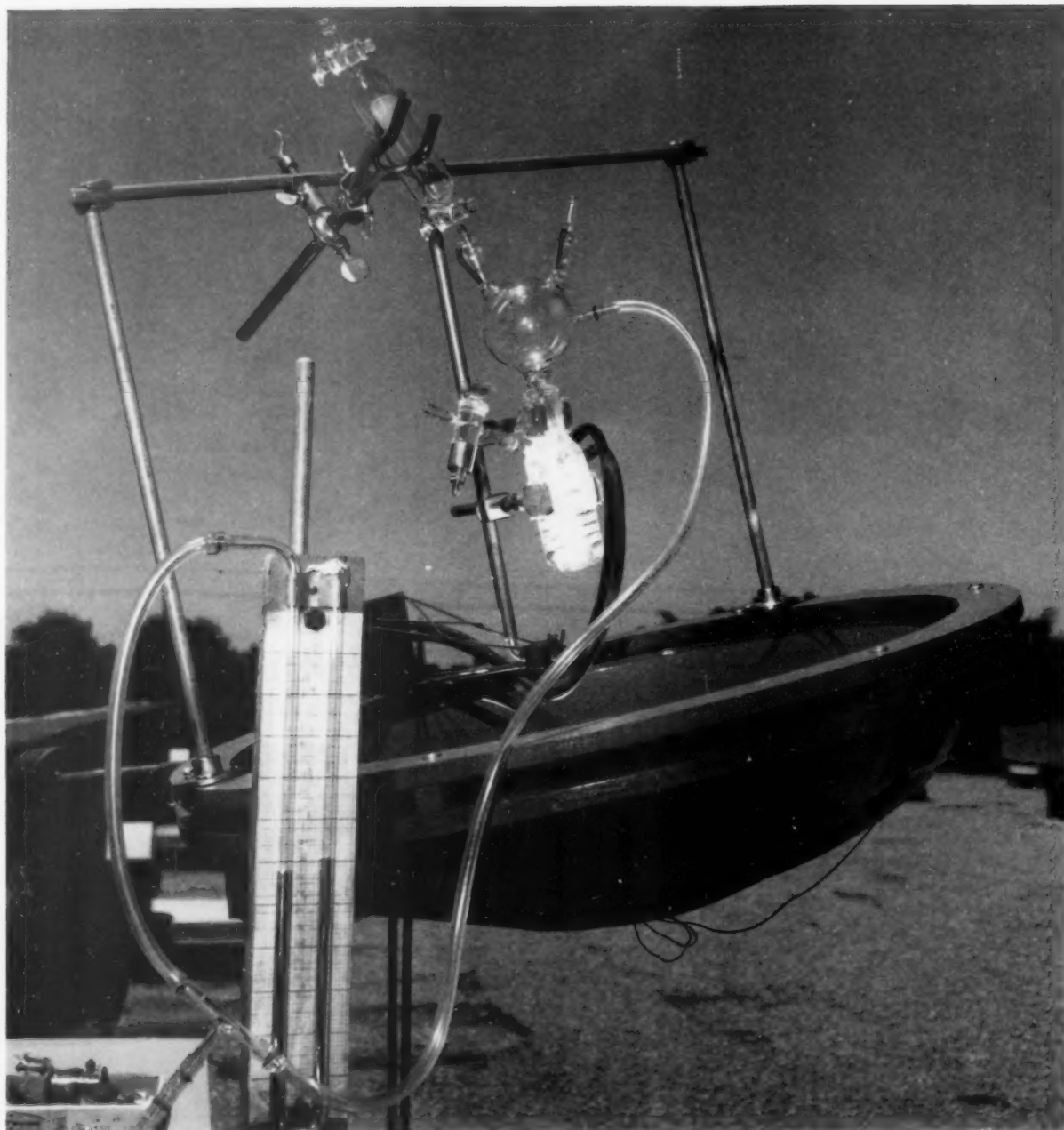
FIG. 1—The Two-Foot Solar Furnace Showing Reaction Vessel E in Position.

pumped through the storage vessels. The cover plate of the concentrating mirror was then removed, exposing the nitrosyl chloride to the concentrated light rays.

Samples of nitrosyl chloride were taken for wet analysis of chlorides (Volhard method) at the start and end of each run. Pressure and temperature readings were taken during the course of all runs. At the conclusion of a run, a gas sample was taken for mass spectrometer analysis.

EXPERIMENTAL RESULTS

1. Static System

Eight runs were completed on the insolation of nitrosyl chloride in carbon tetrachloride at the focus of the two-foot solar furnace. In eight experiments, using the static system (Fig. 2), less than 2% of the initial nitrosyl chloride content was decomposed. This observation was based upon pressure readings and upon the chloride ion titration (Volhard method)
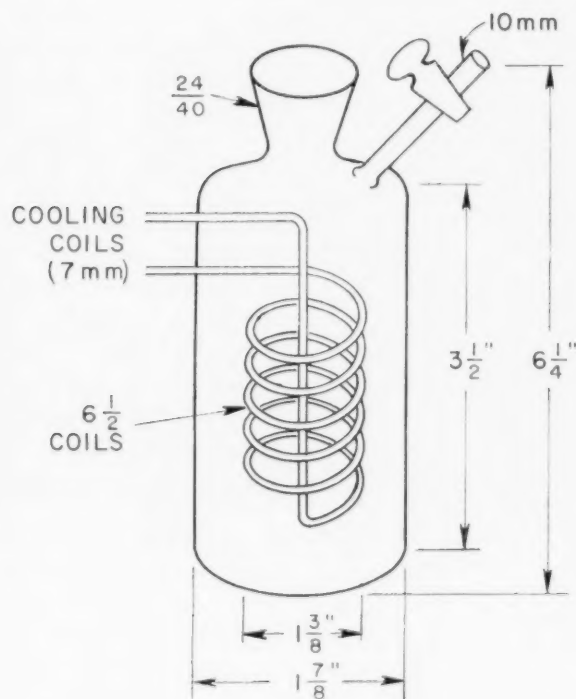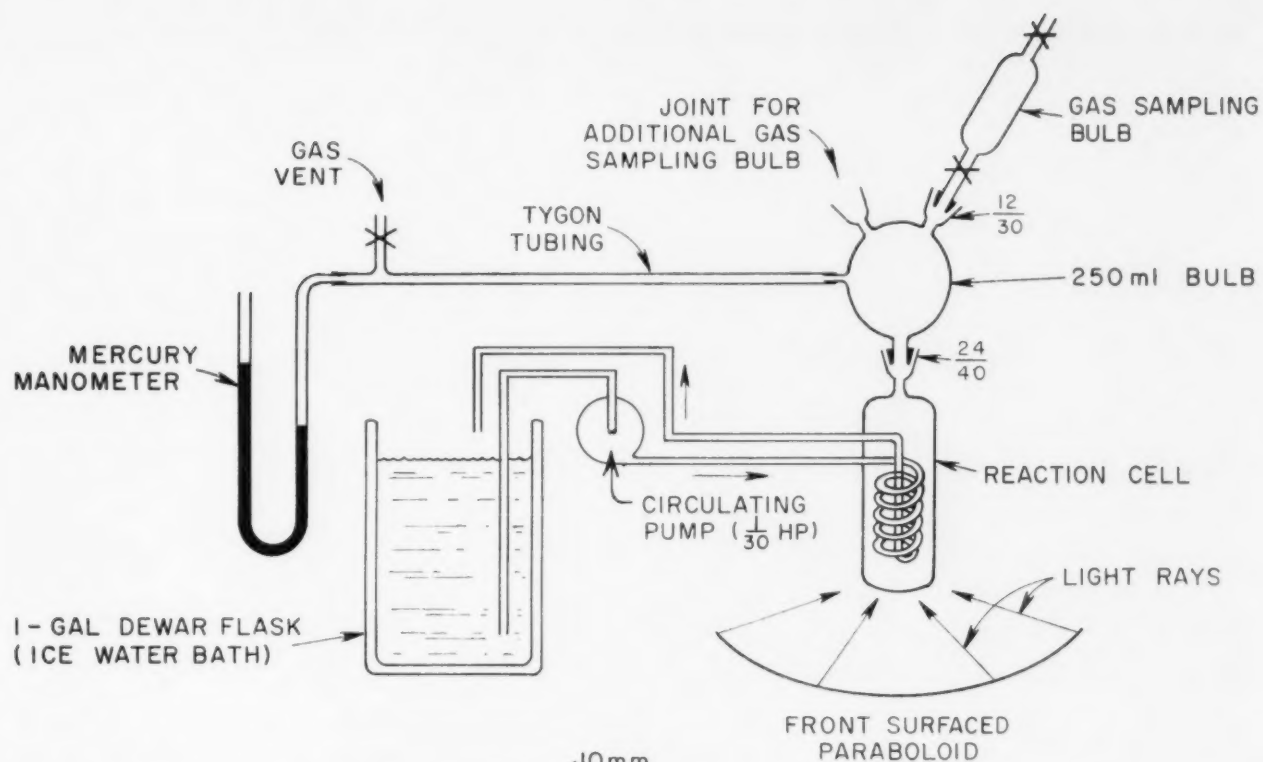
FIG. 2—Reaction Vessel and Monitoring System for Liquid Phase Photochemical Reactions in Two-Foot Solar Furnace: Reaction Cell E.

FIG. 3—Gravity-Feed Flow System with Reaction Cell G in Position.

of the initial and final solutions. The mass spectrometer results were discarded when it was found that nitrosyl chloride decomposed and reacted with metal at the heated inlet of the mass spectrometer.

In one run, an attempt was made to study the recombination of the product gases when the light was shut off. The pressure data from this experiment are graphically presented in Fig. 5. In this graph, the step-wise increase and decrease in pressure are plotted against time as the solar furnace is opened and covered. These results agree with those obtained by Neuwirth[13] with unconcentrated sunlight. During this run less than 5% of the original nitrosyl chloride was decomposed.

2. Open System

In order to minimize the back reaction, experiments were performed in which the reaction cell was left open to the atmosphere so that the evolved gases could escape before recombination could occur. In the open system experiments, reaction cell E (see Figs. 1 and 2) was used without the gas storage and sampling bulbs so that the product gases could escape to the atmosphere. Aliquots of the illuminated solution were taken so that the NOCl concentration could be followed by titration as a function of time. The temperature of the nitrosyl chloride solutions was 30° to 35°C during insolation.

The rate constants for these runs were determined graphically. The first order relationship for three different experiments is presented in Fig. 6. For two of these experiments, the rate constant was found to be 0.0099 min^{-1}; the third experiment, run on a hazy day, resulted in a rate constant of 0.0061 min^{-1}.

It is well known that nitrosyl chloride also decomposes thermally in solution if the partial pressure of the products is sufficiently low. Table I gives some rates in carbon tetrachloride. These are considerably slower than those reported for the gas phase.[16]

The differences between the rate constants for thermal (Table I) and photochemical (Fig. 6) decomposition at the same temperature would indicate the photochemical contribution to the decomposition.

3. Gravity Feed Flow System

Since the amount of decomposition of nitrosyl chloride appears to be seriously affected by recombination of the photoproducts, a start was made on the design of flow systems to be used in the solar furnace. The first such system is a gravity feed flow system shown in Figs. 3 and 4. With such a flow system, it may be possible to minimize or prevent the accumulation of the products, nitric oxide and chlorine.

Twelve runs were completed in which 1000 ml of approximately one molar nitrosyl chloride in carbon tetrachloride were passed through the focal spot of the solar furnace at rates of 50 to 150 ml/min. Based upon the Volhard titration, approximately 3 to 7% of the initial nitrosyl chloride was decomposed. Some difficulty was encountered in keeping the focal spot inside the much smaller reaction cell. Furthermore, the gravity feed was not nearly constant enough for any meaningful interpretation of results obtained hitherto. It is clear that considerable work needs to be done on flow systems before they can be considered to be reliable and useful adjuncts to the operation of the solar furnace as a light source.

DISCUSSION

There is ample evidence that the recombination of nitric oxide with chlorine is fast. Atwood and Rollefson[1] showed that the reaction of nitric oxide and chlorine in the gas phase is so fast that the photostationary state which could be set up by their light source was not measurable. These authors eliminated this back reaction by adding oxygen to form nitrogen dioxide and by using hexane as a solvent to react with the chlorine. Welinsky and Taylor[16] measured the rate constant for the reaction of nitric oxide and chlorine in the gas phase; this third order rate constant was found to be of the order of 10^7 cc^2/mole^2-sec at 35°C.

COLD FINGER

THERMOCOUPLE WELL

$\frac{12}{30}$

GAS SAMPLING BULB

MERCURY MANOMETER

$\frac{12}{30}$

2 LITER FLASK

GAS VENT

TO COLD FINGERS

LIGHT RAYS

FROM COLD FINGERS

FRONT SURFACED PARABOLOID

$\frac{12}{30}$

BYPASS VALVE

2 LITER FLASK

NOTE:
ALL CONNECTIONS MADE WITH POLYETHYLENE TUBING

POSITIVE DISPLACEMENT PUMP

DRY ICE ISOPROPYL ALCOHOL BATH

3cm

2cm

36cm

4.7cm

1.1cm

8mm TUBING

BALL JOINT

1.2cm

BALL JOINT

3.7cm

8mm TUBING

5cm

30cm

31cm

3.7cm

33cm

REACTION CELL	F	G
SYSTEM VOLUME	4400 ml	4500 ml
CELL VOLUME	25 ml	75 ml

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Fig. 4—Gravity-Feed Flow System for Liquid Phase Photochemical Reactions in Two-Foot Solar Furnace: Reaction Cells F and G.
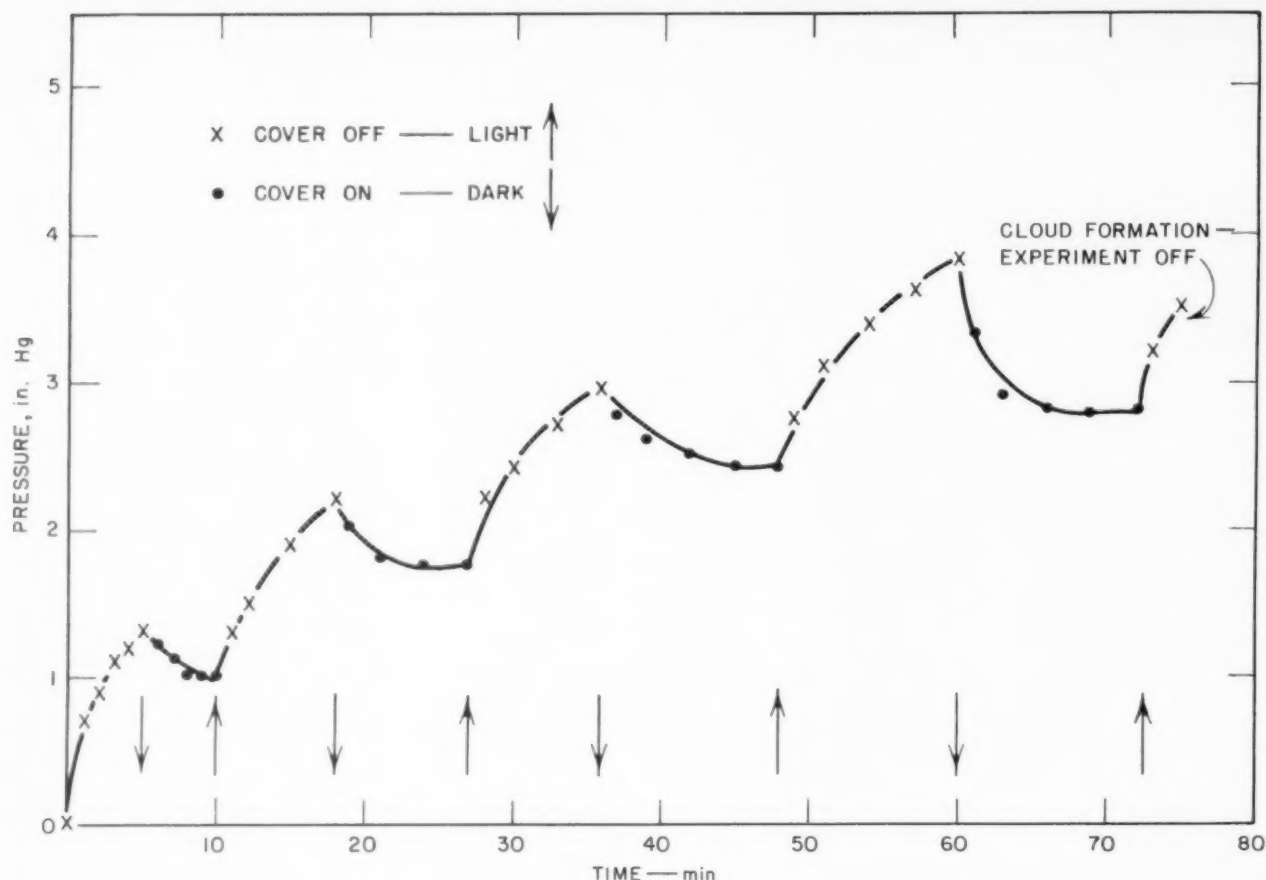
FIG. 5—Effect of Concentrated Light on Decomposition of Nitrosyl Chloride in Static System.

It is of interest at this point to consider one mechanism of decomposition suggested by Kistiakowski[8]:

$$NOCl + h\nu \rightarrow NO + Cl \qquad [4]$$

$$Cl + NOCl \rightarrow NO + Cl_2 \qquad [5]$$
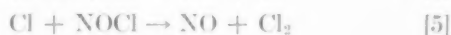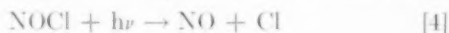
Thus, if the rate constant for the reaction of nitric oxide and chlorine is 10^7 $cc^2/mole^2$-sec in the gas phase, the rate for the recombination of nitric oxide and chlorine atoms (Equation 4) should be even faster since the combination of the two free radicals should have little or no activation energy. Finally, a faster rate of recombination in solution is favored by the Frank-Rabinowitch cage effect which prevents the escape of nitric oxide and the chlorine atom produced inside a cage of solvent molecules.

Trautz and Gerwig[15] noted that the kinetics of the liquid phase reaction are about what might have been expected from extrapolation of gas phase data. Noyes[14] found that the reaction between nitric oxide and liquid chlorine, or chlorine dissolved in carbon tetrachloride, was rapid at $-80°C$ and that the rate was still appreciable at $-150°C$. These fast rates were also observed by

Boubnoff and Guye.[2] Further, Kiss[7] showed that the recombination took place in the dark.

Thus, the use of the nitrosyl chloride reaction as a means of storing energy is dependent upon a method of preventing the recombination of the product gases, nitric oxide and chlorine. Two such methods can be suggested. One would be a flow system in which the product gas is taken off quickly after the photochemical dissociation. We have taken some steps in this direction, but considerably more work is needed to find a satisfactory flow system for use with the solar furnace. Another method of preventing recombination would be use of a solvent which makes one of the products (presumably chlorine) unavailable. Such a solvent should be capable of giving up the chlorine upon de-

TABLE I

Temp. °C	Reaction rate, min⁻¹
40	0.00267
27	0.00096
3	0.00028

+0.2

+0.1

0.0

−0.1

−0.2

−0.3

−0.4

−0.5

−0.6

−0.7

−0.8

−0.9

−1.0

log (a−x), NOCl REMAINING, moles / liter

× EXP 48; SLIGHT HAZE

● EXP 49; SLIGHT HAZE

■ EXP 50; HEAVY HAZE

$k_1 = 0.00989$ min^{-1}

$k_1 = 0.00987$ min^{-1}

$k_1 = 0.00605$ min^{-1}

0   20   40   60   80   100   120   140   160   180

TIME — min
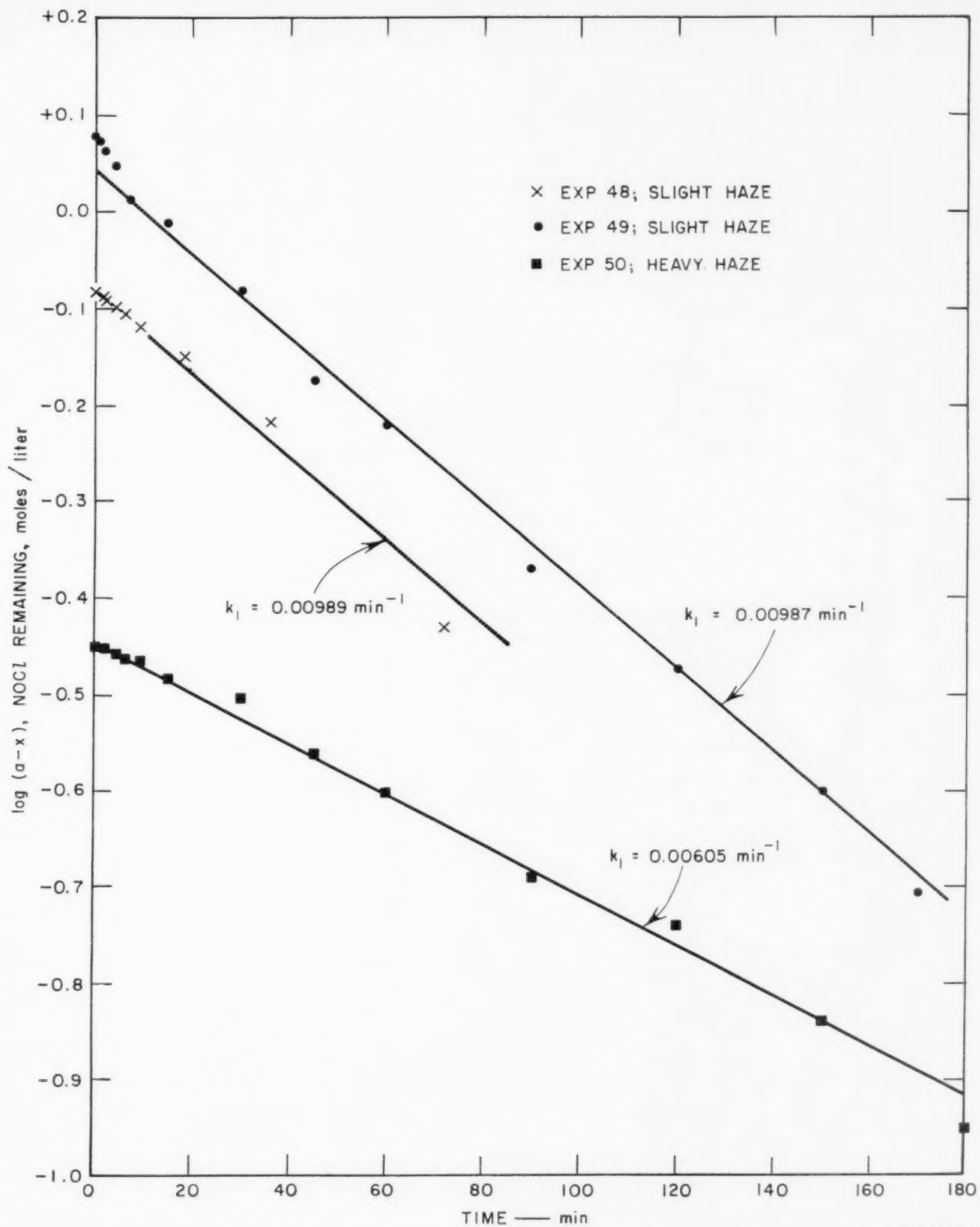
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FIG. 6—Rate of Decomposition of Nitrosyl Chloride in Open System.

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mand when it is desired for recombination, but not before then.

ACKNOWLEDGMENT

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Profits in Solar Energy[*]

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Solar energy applications are examined from the point of view of their profit-making potential. The study is based on a consideration of the availability and characteristics of solar energy, the sources of profit in conventional energy sources, and the type of industry which could participate in the commercialization of solar energy. Solar equipment now being manufactured is of four types—water heaters, batteries, cookers, and toys and novelties. Three types of solar energy equipment now in the development stage are seen to have early commercialization prospects. The largest market during the present century will likely be residential heating and cooling systems. Technical or economic considerations will limit several applications such as commercial electricity from solar energy and capture and storage by photochemical means.

INTRODUCTION

In the past few years there has been a remarkable advance in the stature of solar energy, and scores of talks on the subject are being presented each year by the leaders in this field in the United States and abroad. Most of these discussions appear to survey the numerous possible uses for solar energy and to outline our present technical knowledge in the several fields in which solar energy is most likely to become important. Considerable material on the economics of solar energy use has also been presented. But very little has been said about the profit potential in solar energy. Since this is the primary force and incentive behind all commercialization efforts, it is important that we consider when, how, and by whom are profits to be made in solar energy.

SOLAR ENERGY AVAILABILITY AND CHARACTERISTICS

Before examining the profit possibilities in solar energy, let us take a quick look at this energy source itself. In comparison with practically all of our conventional sources, solar energy is characterized by immense quantity, universal availability, very low concentration, and extreme variability. Its magnitude can be readily appreciated by comparing the national energy consumption of approximately 15 trillion horsepower hours per year with the annual solar energy received, amounting to 25,000 trillion horsepower hours. The solar energy supply is thus about 1,700 times as great as our present energy needs. In comparison with world reserves of fossil and nuclear fuels, the solar energy input is so great that all of the world's known fuels would last only a few days if they were used to produce heat at a rate equal to our solar input. Or, in more easily-visualized quantities, a Texas oil well on a quarter section of land would have to produce crude oil at a perpetual rate of 2,500 barrels per day to have an energy output equal to the sunshine falling on that piece of ground.

Although solar energy is universally received, quantities vary considerably. In the far northern and southern latitudes, the annual input is less than one-fourth of that received in a sunny temperate zone. Besides latitude factors, atmospheric conditions may reduce annual average energy receipt by substantial percentages. Typical annual average radiation intensities in very sunny climates are around 2,000 Btu per day per sq ft of ground area. A mean value for the entire United States is approximately 1,500. In London, the annual average is only about 900.

These figures illustrate, also, one of the two major drawbacks in the utilization of solar energy. To convert solar energy to another form for use, some sort of surface must be used to intercept the radiation and convert the radiant energy to another form such as heat, electricity, or chemical compounds. Conventional energy-exchange surfaces, such as the tubes in a boiler furnace, may have hourly heat rates of 100,000 Btu/sq ft of surface, and seldom would a commercial heat exchanger be operated at heat-transfer rates below a few thousand Btu per hour. Solar radiation, however, has a maximum intensity of only about 350 Btu per sq ft per hour, and, on the average, in a sunny climate, only about 200 Btu would be available er sunshine hour on each square foot of heat-transfer surface. This means that large surfaces must be used for the recovery of appreciable quantities of energy.

Possibly the most serious drawback in the utilization of solar energy is its intermittent nature. Not only is there the regular and predictable variability from day to night, but there is fluctuation due to cloudiness. Seasonal variability is superimposed on these other fluctuations. The use of solar energy would thus have to depend on there being (a) no need for continuous energy supply, or (b) supplementary energy availability when solar energy is unavailable, or (c) the availability of some form of solar energy storage. Examples of the first situation are very scarce; in the second situation there is promise of use; and in the third situation there has been considerable use.

SOLAR AND CONVENTIONAL ENERGY SOURCES

In approaching the question of profit in solar energy, it may be helpful to consider the sources of profit in conventional energy supplies. By so doing, we may see more clearly what types of industry should participate in the commercialization of solar energy.

Those firms and individuals who have income from energy may be divided into three groups. First, there are the owners and producers of the basic energy source. These comprise the organizations which own and mine coal and uranium deposits and those who own, discover, produce, and sell petroleum and natural gas. Secondly, there are the organizations which convert the basic energy sources to other forms and sell the resulting energy. These include the petroleum refiner who manufactures motor fuel, furnace oils, and so on, and the utility companies which produce and sell electricity by burning the basic fuels or by using water power. And thirdly, there are the suppliers of materials and equipment which are used by the producers, the converters, and the ultimate users of energy. Included here are the manufacturers of automobiles, electric generating equipment, steam boilers, household furnaces and air conditioners, cook stoves, and the many materials which go into the fabrication of such pieces of equipment.

Let us now see how solar energy might fit into this pattern of organization in the energy industry. At once, it is clear that there is no counterpart of the owner and producer of basic fuel energy. Although land-grabbing on the moon may not be far off, there is not much thought about staking out claims on the sun. So every land owner is in effect a sun owner, in proportion to his acreage. As a result, there appears to be no profit potential in the energy owner and producer category of industry.

Next, in converting solar energy to forms which are saleable, there is not yet, but there probably ultimately will be, the public utility which will generate electricity from the solar source. The purchase of adequate land

and the construction of solar heat-recovery equipment will put the public utility in a position in the solar energy field entirely analogous to that which it now occupies in the use of fuels for the same purpose. As explained later, however, this is a long-range development of little immediate potential in the United States.

It is in connection with the supply of materials and equipment for solar energy conversion that industry can profit from solar energy as it now does from other energy sources. The conversion of solar radiation to heat or to work or to some other form of energy requires facilities analogous to those presently being used in the conversion of energy from other sources. The heating of houses will require solar collectors, heat-storage units, and control systems; these in turn will require metals, glass, plastics, chemicals, and so on. Solar power plants will require the usual power-plant equipment along with special facilities for producing steam from radiation; direct conversion of solar energy to electricity will require semiconductor, alternator, and transformer equipment. Even solar toys involve the producers of materials and equipment.

There are no owners of solar energy, so its use cannot be expected to receive the sort of promotion that natural gas does, for example. Thus one incentive for solar energy development is lacking. In the category of converters and sellers of energy, there is a corresponding lack of incentive to develop solar energy because there are ample and, in most cases, cheap supplies of fuel and water power for conversion. An alternate basic supply is not yet needed, and the time when it may be needed is too distant to justify research and development expenditures by these organizations now. To some extent, the same might be said of atomic energy, but here there is a heavy government subsidy to the developers of this source which is absent in the case of solar energy.

Since only one out of the three types of industries concerned with energy supply will participate in solar energy profits in the near future, the probable rate of development of this resource will be largely dependent on the efforts of those manufacturers of energy-conversion equipment and their material suppliers. Research and development will undoubtedly be concentrated among these firms and carried forward at rates dependent on the profit and sales potential of the products. Inasmuch as heat and electricity from a solar source are no different from these energies when derived from conventional fuels, the substitution of solar energy is dependent almost exclusively on economic factors. The ultimate energy derived from solar radiation must be competitive in cost if suppliers of conversion materials and equipment are to sell their products. In the final analysis, then, the rate of solar development by equipment and material suppliers de-

pends on their ability to develop and produce such goods which will make the converted energy competitive with that from conventional sources.

If public utilities will not be using solar energy equipment for many years to come, who are the buyers for solar conversion equipment? The purchase pattern appears to be largely built around the individual user—the home owner, the business man, the industrial firm, and the farmer. These individuals and groups have solar energy available to them; they will purchase the equipment to convert this energy to useful forms, and they will then utilize the heat, electricity, or other products derived therefrom. Ultimately, the commercial power supplier will also be an equipment customer, but the principal market is, and for some time will be, the individual user of converted solar energy.

WHAT MANUFACTURERS ARE ALREADY PROFITING FROM SOLAR EQUIPMENT SALES?

Solar energy equipment now being manufactured and sold may be conveniently discussed in four principal groups: solar water heaters, solar electric converters or "solar batteries," solar cookers, and toys and novelties. These products are made by numerous manufacturers, who need materials which must, in turn, be supplied by the makers of metals, plastics, glass, and so on.

The manufacture of domestic solar water heaters in Florida has been going on for several decades. Comprising simply a blackened metal sheet, about 50 sq ft in area, in contact with tubing through which water circulates and above which one or two glass plates are mounted to reduce heat loss, these roof-mounted units can supply enough warm water for an average household in southern Florida. An insulated storage tank above the solar heat exchanger or "collector" permits gravity circulation to the heating panel and stores hot water for nighttime use. Some systems employ a pump and storage tank below the heater. A recent survey shows no less than a dozen sizable manufacturers of this equipment and that approximately 25,000 solar water heaters are used in this area. Recent developments in insulation, heat-transfer surfaces, and transparent plastic films may stimulate this market considerably.

Almost at the other extreme of size and precision are the solar cells being manufactured for use in radios, clocks, toys, hearing aids, and communication equipment. Although the scientific principle has long been known, a commercial photoelectric device for net electricity production did not appear to be practical until a few years ago, when the Bell Telephone Laboratories developed the silicon cell. This development gave promise because of the much higher efficiency

obtainable with the silicon cell than had hitherto been possible with other types.

When a very pure crystal of silicon is sliced into thin wafers which are then "doped" with traces of certain other elements, the semiconductor structure produced results in a current flow when the wafer is exposed to sunlight. With suitable electrical connections, electricity can be delivered from these cells at an efficiency in excess of 10 per cent. Since the wafers have an area of less than one square inch, many would be required for delivery of much motive power; but energy for communications and other small power needs can be obtained from a relatively few irradiated cells. The Hoffman solar radio, for example, needs only half a dozen. The satellites this country has launched have radio equipment powered by these solar converters.

At present prices of silicon metal and solar cells, a kilowatt of generating capacity would cost over $50,000. But there are interesting possibilities for substantial cost reductions, such as the use of focusing reflectors to concentrate considerable solar energy onto comparatively few solar cells and the use of less expensive methods for preparing the silicon surface. But even if the solar cell remains an expensive source of kilowatt hours, there will be many new uses for small electrical outputs at these costs. Electricity in space and on the planets may well be produced primarily by converters of this type.

In the third group of products, the solar cooker is beginning to yield profits for the manufacturers of sports equipment. At least three different styles are being commercially made at the present time. The one with which the author is directly concerned is a folding type of solar barbecue grill which focuses the sun on the cooking surface by means of a flexible fabric-plastic reflector supported on a modified umbrella frame. Heat is delivered to the grill at a rate of nearly a kilowatt or about 3000 Btu per hour. Meats can be broiled or barbecued on the Umbroiler in less time than it takes to get charcoal well started, and a camper's sunheated coffee pot can often be boiling over before his companions can collect firewood. The multi-million-dollar business of the makers of charcoal barbecue units will undoubtedly stimulate further commercialization of solar cooling equipment.

Still another group of solar energy operated devices are making profits for the manufacturers of toys and novelties. Two examples are the solar cigarette lighter and the radiometer toy, formerly seen only in optical store windows. The lighter is a 5-in. aluminum dish which concentrates the sun on a cigarette held at the focal point; the revolving pinwheel toy operates by absorbing enough sunlight on the blackened sides of its vanes for them to receive little pushes from heated gas molecules occupying the space in the glass bulb.

The solar energy equipment now being sold requires a considerable variety of raw materials and auxiliary products. Demands for these are relatively small in comparison with other requirements for glass, metal, plastic films, insulation, fabrics, electronic equipment, and so on. But the present modest scale of commercialization of some of these products is probably only a forerunner of greatly enlarged future markets. Material demands will naturally enlarge as equipment sales grow.

With the exception of solar electric cells and solar toys, all of the present commercial solar energy products supply heat. Moreover, the major new applications foreseeable in this century will also utilize solar energy for heat supply. This situation reflects, in part, the technological problems involved in converting solar radiation to mechanical forms of energy.

Another characteristic of these applications is their domestic nature. Since the principal equipment customers are individual families, distribution and selling are important factors in the marketing of solar devices. These activities involve also the sales appeal of the product and advertising. As with many other consumer products, successful solar development may not demand fully competitive energy prices provided that substantial sales effort is put behind the product.

ADDITIONAL PRODUCTS WITH EARLY COMMERCIALIZATION PROSPECTS

There are three types of solar energy operated equipment in the development or testing stages which may soon become items of commerce. It appears that their application will first be limited to other countries where domestic sources of energy are scarce and expensive or where drinking water is difficult to obtain. These items are a domestic food cooker, a solar energy operated food refrigerator, and a small solar distillation unit for demineralizing highly saline water.

Reflecting-type solar cookers of rigid plastic with reflective metallized linings have received field trials in Mexico and in a few other countries where firewood for cooking has become a critical problem. Potentially cheap, these units show promise for substantial sales and use in parts of Mexico, Central and South America, Southern Asia, the Middle East, and North Africa. Tests have shown that these cookers are sturdy, durable, and adaptable to the cooking habits of peoples in many of these areas.

Simple food refrigerators intended for use by peoples in these same regions, often where domestic refrigeration is unknown, are being developed for use in combination with solar cookers. By means of a simple intermittent absorption cycle, several pounds of refrigerant and absorbent in a two-chambered metal container can keep a small insulated "ice-box" cold for 24 hours. The unit must be regenerated once a day by solar

heating for about two hours. At a price potentially below $25, the market for such a unit might be in the many millions.

A third need of many persons in the arid, unindustrialized regions of the world is safe drinking water for themselves and for domestic animals. In many areas, highly saline ground water is available but practically unusable. Other areas, many with high populations, are right on the sea coast but lack fresh water even for absolute minimum requirements during certain seasons. Low-cost water distillation equipment would find ready application in these regions, provided that operating energy is available.

Recent improvements on a century-old design, in respect to materials of construction, design, and fabrication technique, show promise of bringing equipment costs down low enough so that, with free solar energy, demineralized sea water and brackish water can serve these drinking water needs. By evaporation in glass-covered shallow basins directly heated by the sun and condensation on sloping glass covers, distilled water can be produced from sea water in a sunny climate at a daily rate of approximately 0.1 gal per sq ft of basin. This design is now being tested at a pilot plant in Florida, and other units employing transparent plastic films in place of glass are being constructed and tested. As designs are simplified and costs reduced, small installations should begin to appear in areas where water is a most critical problem. As water demands rise and solar distillation costs are further reduced, markets for the units and their materials of construction should undergo substantial expansion.

The identity of the ultimate marketers of solar distillation equipment is not yet clear. One possibility is that plants will be built in the field by construction contractors, basic materials being purchased for fabrication and assembly at the site. Another possibility is that complete prefabricated units, particularly of the plastic type, will be sold as an item of commerce. This arrangement will probably apply, in any event, for small, family-sized units of a few gallons daily capacity.

MAJOR FUTURE MARKETS FOR SOLAR ENERGY EQUIPMENT

By far the largest markets for solar energy equipment, at least during the present century, will be for residential heating and cooling systems. One-fourth of the nation's energy consumption is for space heating, and a steadily increasing fraction of electrical output is used for air conditioning. Substitution of solar energy for these uses, even if initially only in the sunnier regions of the country, will require huge quantities of solar heating and cooling equipment.

Residential solar heating is still in the development stage. At least five structures in the United States are

now partially heated by solar energy and others are in the planning stage. Several different systems are being used. One employs hot water in a manner similar to that of the Florida water heaters previously described. Larger solar energy receivers and hot water storage tanks are employed. Supplementary heat is being supplied either by conventional furnace equipment or an air-source heat pump. Other systems employing hot air have been built, including that of the author's home in Denver. Here, air is heated by passage between partially blackened glass plates exposed to the sun. Storage is accomplished by passing the hot air through vertical, gravel-filled cylinders in which the air delivers its heat to the rocks. The house is heated by circulating air through the heated rock bed. In still another system, comparatively low-cost chemicals are used for heat storage by means of their heat of fusion.

The present solar-heated homes in Massachusetts and Colorado and two solar-heated commercial buildings in New Mexico and Arizona are yielding valuable information on equipment performance, architectural design, convenience, economy, and public acceptance. All these factors and others are important.

In areas where domestic fuel is cheap, solar heating will probably not find a significant market in the near future. Elsewhere, particularly where fuel costs are rising rapidly and where sunshine is plentiful, there should be commercial applications within a very few years. Economic factors are not now favorable for the construction of individual solar heating systems, but with factory-production of solar heating equipment, costs should become competitive with fuels in many areas.

The development of solar powered air-conditioning equipment is considerably behind that of solar heating equipment. No full-scale units are yet in operation. But the appealing aspects of maximum energy availability coincident with maximum cooling demand, seasonally and even almost hourly, along with the rapid growth of domestic air conditioning, are stimulating research in this field. Most attractive are absorption refrigeration systems operated by hot water, air, or steam supplied from roof-mounted solar heat exchangers used also for winter heating. Delivery of heated fluid at temperatures around 200°F. can readily be accomplished by the use of existing solar heat-exchanger designs. The technical problems are more formidable than those of the heating system, but the favorable annual load factor on solar equipment operating most of the year is a strong development incentive.

It is very difficult to estimate the potential market for solar heating and cooling equipment. But even if as little as ten to fifteen per cent of new residential con-

struction is provided with solar heating and/or cooling systems, the annual market for perhaps 200,000 units could gross nearly half a billion dollars for the manufacturers of this equipment. Substantial application of solar heating and cooling will also involve other industrial suppliers such as the manufacturers of control equipment, pumps, blowers, motors, and other accessories. Large new markets for glass, metals, heat-exchanger equipment, insulation, and other materials will be established.

Some recent new solar developments may accelerate the rate of domestic application considerably. One of the most significant is the selective radiation surface which, by means of a thin oxide film on a polished metal, yields high absorptivities for solar radiation and low emissivities for thermal (lost) radiation. Other developments are improved plastic films with high strength and long life which could supplement glass in some applications, improved insulation materials, better caulking compounds, and so on.

In an over-all view of residential heating and cooling with solar energy, we can see that (1) these uses represent a large segment of the national energy demand, (2) energy costs are rising and will continue to do so, (3) the quantity of solar energy available in winter and summer in most areas of the country is adequate for most of the house heating and cooling requirements, and (4) the architectural, technical and economic factors can be favorable to this development.

LONG-RANGE APPLICATIONS

Because of technical as well as economic limitations, several important applications of solar energy appear to be for the future rather than the present. Commercial electricity from solar energy, for example, appears to be limited primarily by *costs*, at least insofar as presently known methods for conversion are concerned. The efficient capture and storage of solar energy by means of reversible chemical reactions, on the other hand, has not yet been achieved because of *technical* problems.

The conventional approach to electricity from solar energy is by operation of an engine by means of steam produced at the focus of a concentrating solar reflector. These reflectors have various shapes, such as paraboloids, parabolic cylinders, and circular cylinders. Steam has been produced in a small circular boiler, in a long tube at the axis of a parabolic cylinder, and, more recently, in a flattened tube at the focus of a circular cylinder. The high cost of these reflecting surfaces, necessarily movable to follow the sun, and the very low efficiency of steam engines operating at only moderate pressure have made the fixed cost of the installations per kilowatt-hour generated much greater than the cost of electricity from large conventional power plants.

Another and possibly more promising approach is the vaporization of water or some more volatile liquid in flat-plate solar heat exchangers similar to the units used for house heating. The use of selective radiation surfaces and glass covers treated to minimize reflection enhances these possibilities. But major cost reductions will have to be made before this source of electricity can begin to compete with modern power plants. Again, however, in parts of the world where fuel is very expensive, small electric generating plants operated in this manner should eventually become important. Then, as fuel costs continue to rise elsewhere, and nuclear-energy costs rise also, solar electricity will gradually become predominant.

The other route by which large-scale electric power may be produced from solar energy is by direct conversion with semiconductor materials such as are employed in silicon cells. Economies in materials, manufacture, and utilization will certainly reduce the cost of this type of equipment. Actually, this source of power has much further to go than does the solar-exchanger heat-engine cycle to meet competition from fuel. With present solar cell power at a cost about ten times as great as electricity from dry cells, major developments will be needed. These are certainly not out of the realm of possibility.

Another development of major potential in solar electricity generation involves the recent improvements in thermoelectric materials. Although solar heating of thermoelectric elements had previously been tested, power outputs were so low that the method appeared to have very little promise. But the introduction of semiconductor and insulator-like thermocouples having high thermoelectric power as well as the ability to withstand high temperatures has raised the best heat-to-electricity efficiencies above 10 per cent. With the possibility of even further improvement, the heating of a thermoelectric element at the focus of a solar reflector appears to be a promising technique for electric power generation. Research is therefore proceeding in this area.

These discussions of possibilities for the entry of the public utilities into the production and sale of solar electricity are based on considerations of only the presently known practical sources of energy. If successful and reasonably economical power can be achieved from the nuclear fusion reaction, based on hydrogen or deuterium, commercial solar electricity may be delayed many centuries. Certainly no one is able to make such distant projections, so the best we have been able to do is to outline the expected situation *if* factors preclude application of this vast source of energy.

No solar energy discussion would be complete without mention of the remarkable capabilities of the solar furnace. With very precise focusing reflectors ranging in size from a few feet in diameter to the great 35-ft French solar furnace, these systems can produce temperatures in excess of 5,500°F. The newest solar furnace installation is at the Quartermaster Research and Engineering Center in Massachusetts, where a 28-ft-square composite focusing mirror can develop temperatures of 4,000°F.

Although these units have some unique research and development uses, their cost now prohibits their application as industrial production equipment. Another long-range prospect, therefore, is that solar furnaces of perhaps more economical design will be used for special high temperature metallurgical and ceramic processes. Solar variability would of course be a disadvantage, but choice of furnace sites could minimize unplanned shut-downs.

One of the most intriguing potentialities of solar energy is in combined energy absorption and storage by means of photosynthetic chemical reactions. For example, in the presence of certain catalysts, water can be decomposed into hydrogen and oxygen by the absorption of energy in the ultraviolet portion of the solar spectrum. These gases can be stored for subsequent combustion and power generation. Certain other aqueous reactions could possibly be utilized whereby absorption of energy would cause a change in one direction which could then be reversed when desired to liberate the absorbed energy as heat or, more ideally, as electrical energy. Limited progress has been made along some of these lines, but, as yet, efficiencies in converting solar to chemical energy of only small fractions of one per cent have been achieved. If a substantial technical breakthrough should occur along some such line, the whole economic picture of large-scale solar-energy utilization could be affected. Mechanisms of suitable reactions, a complete understanding of natural photosynthesis, and other basic problems will probably have to be solved before substantial headway is made into practical application of these principles.

This brief discussion of long-range solar energy possibilities has departed somewhat from the subject of profits in solar energy. At least, these fields do not appear to have profit potential within the next several decades. However, these possibilities should be kept in view so that advantage may be taken of even small steps forward in these and related fields.

CONCLUSIONS

In the broad view, solar energy potentially has all the applications of conventional energy sources. There are some considerable differences in the incentives for development of this new source, the primary responsi-

bility for which will rest with the manufacturers of materials and equipment used in the conversion of energy from one form to another.

Several products are already being made and profitably sold to individual users for converting solar energy to heat and for small electrical applications. Water heaters, cooking units, toys, and solar cells represent this group. On the horizon are several domestic products such as cookers, refrigerators, and water distillers for use in other parts of the world where energy is expensive.

The major profits in solar energy equipment and ma-

terials, as far as the next few decades are concerned, will be in house heating and cooling equipment. In active development now, these applications will take place at an accelerated rate as production economies are achieved and domestic fuels become more costly.

Profits for the converters of energy, that is, the public utilities, in the generation of electricity from solar energy are decades away in the United States. Prior use will undoubtedly occur in areas of the world having less abundant fuels. Photochemical conversion and other long-shot solar applications are research challenges for the future.

A Simple Reaction Turbine as a Solar Engine

By B. S. Leo* and S. T. Hsu†

Theory and experimental data of a simple reaction turbine were presented in an earlier issue of this journal.[1,2] This article describes the design improvement and performance of the reaction turbine when operating under vacuum conditions. A method of distilling water and obtaining power simultaneously by using a closed cycle is presented. Also thermo-electric and thermionic power sources are discussed.

Improvement in Turbine Design

The design of the reaction turbine was simplified by eliminating the shaft and pillow blocks and by placing a disk between the two shields for easier balance. The new design of the turbine is shown in Figures 1 and 2.

This turbine is simply a statically balanced disk with a hub, which can be mounted on a pump or generator shaft by tightening the two set screws. Both manufacturing cost and weight have been reduced. The weight is 6.5 lbs compared with 43 lbs for the first turbine and the cost is less than ten dollars.

The combination of turbine and pump is shown in Figure 3. This combination gives a more compact unit than the previous one.

The Vacuum Chamber

Operating the turbine under vacuum conditions has two advantages. The first is a greater enthalpy drop across the nozzle, giving a higher exit velocity. And the second is a reduction in windage loss of the turbine due to the decrease in density of the surrounding medium.

To prevent usage of power from the turbine and to obtain and maintain a vacuum, the turbine and pump must be enclosed and a vacuum created by flushing out the air in the enclosure with steam; which is then condensed. Preliminary tests showed that a vacuum of 25 inches of mercury could be reached without difficulty by this method. The exhaust steam from the turbine has to be condensed to keep the vacuum.

The optimum turbine diameter when operating

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under vacuum conditions was determined by the method described previously.[1] It was found that a one foot diameter turbine develops the maximum horsepower for the speed range 0–10,000 rpm.

A simple vacuum chamber was constructed by using a 15 in diameter steel tube with a wall thickness of $\frac{1}{4}$ in. The condensate from the chamber is collected in the condenser, which is a steel container with a volume of 0.5 cu ft. The piping is $\frac{1}{4}$ in steel pipe. The arrangement is shown in Figures 4 and 5.

The vacuum is created by opening valves (1), (4), and (5) to flush out the air in the condenser and chamber with steam from the supply line. The valves (1) and (5) are then closed and the steam in the condenser and chamber is condensed. The vacuum in the condenser and chamber is indicated by the gage mounted on the front end of the chamber. A vacuum of 26 inches of mercury was reached in this manner without any difficulty.

TEST RESULTS

The turbine is started by opening supply valve (3) until a pressure of 35 psi is read on the gage in the supply line.

The performance of turbine and pump was excellent. Only a very slight vibration was felt in the vacuum chamber. The noise from the exhaust jet of the turbine was damped out by the chamber walls so that only a very slight humming was detectable. The turbine pumped 1000 gal of water per hour against a head of 12 ft using 25 lb of steam per hour at 98 per cent quality and 50 psia pressure compared with 730 gal against the same head when operating non-condensing and exhausting directly to the atmosphere, using steam of the same amount quality and pressure.

The exhaust from the turbine nozzle is condensed when impinging on the inside wall of the chamber, which is cooled by bleeding a small amount of water from the discharge line of the pump and directing it over the turbine exhaust area. Figure 6 shows the the arrangement when pumping against a head of 12 ft.

It was possible to reach a vacuum of 26 in of mercury in about two minutes when the steam was condensed by spraying the condenser and chamber with water. Seven gallons of water at 46 F was necessary to reach this condition within the two minute period.

CONVERGENT DIVERGENT NOZZLE
SHIELD
DISK
TEFLON SEAL
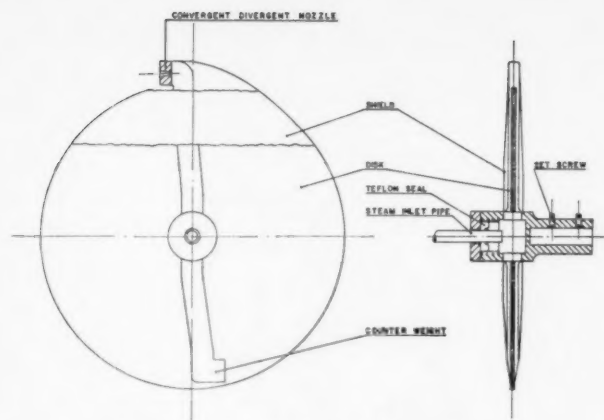STEAM INLET PIPE
SET SCREW
COUNTER WEIGHT

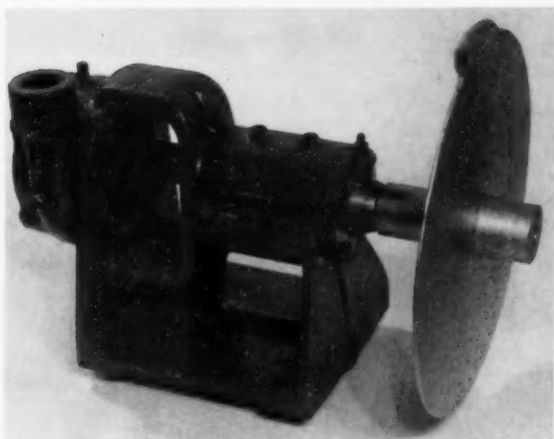FIG. 1—New Design of Reaction Turbine

FIG. 2—Reaction Turbine

FIG. 3—Combination of Reaction Turbine and Pump

The same vacuum could also be obtained without using water by letting the condenser and chamber lose heat directly to the surroundings. The time required for this procedure was 25 minutes with an ambient air temperature of 80 F.

It was possible to hold a steady vacuum between 26 and 22 in by emptying the condenser every half or three quarters of an hour. The turbine did not have to be stopped to empty the condenser. It was only necessary to close valve (4), open valves (1) and (2), and flush out the condensate in the condenser. Valves (1) and (2) were then closed, and the steam was allowed to condense in the condenser. Valve (4) was then opened to drain the condensate from the chamber to the condenser.

About one pound of steam was used to obtain the 26 in of vacuum, and 16 gal of water per hr was bled from the discharge line of the pump and used to condense the exhaust steam from the turbine.

The combination of turbine and pump was in operation intermittently for 50 hr. Both turbine and pump performed very well and no maintenance was required. No difficulties were encountered in starting the turbine and pump after they had been idle for periods of one to two months.

The vacuum chamber and condenser can easily be transported by two persons. The assembling of chamber and condenser requires very little mechanical skill.

The Closed System

The arrangement shown in Figure 4 can readily be connected to a solar boiler to obtain a closed cycle. The steam generated in the boiler flows through the supply line to the turbine where it expands through the nozzle to 5 psia in the vacuum chamber and condenses. The condensate flows to the condenser by gravity since the condenser is at a lower level than the vacuum chamber and the pressure in the condenser is equal to the pressure in the vacuum chamber. The condensate in the condenser is forced back to the boiler by closing valve (4) and opening valve (1) to equalize the pressure in boiler and condenser. Valve (2) is then opened and the condensate flows back to the boiler by gravity, since the boiler is at a lower level than the condenser. The steam in the condenser is condensed and valve (4) is opened again when the pressure in the condenser equals the pressure in the vacuum chamber.

The turbine does not have to be stopped to perform these operations because the vacuum chamber can be designed to hold the small amount of condensate that will collect on the bottom during the time it takes to empty the condenser.

The arrangement of vacuum chamber with turbine and pump can be improved by designing it in such a way that the pump, turbine, and chamber is one complete unit.

Reaction Turbine Using Freon 113

A number of calculations were made to determine if there is an advantage in using Freon 113 for a working fluid instead of water.

The calculations are based on the following data: the Freon leaves the boiler in the saturated state at 165
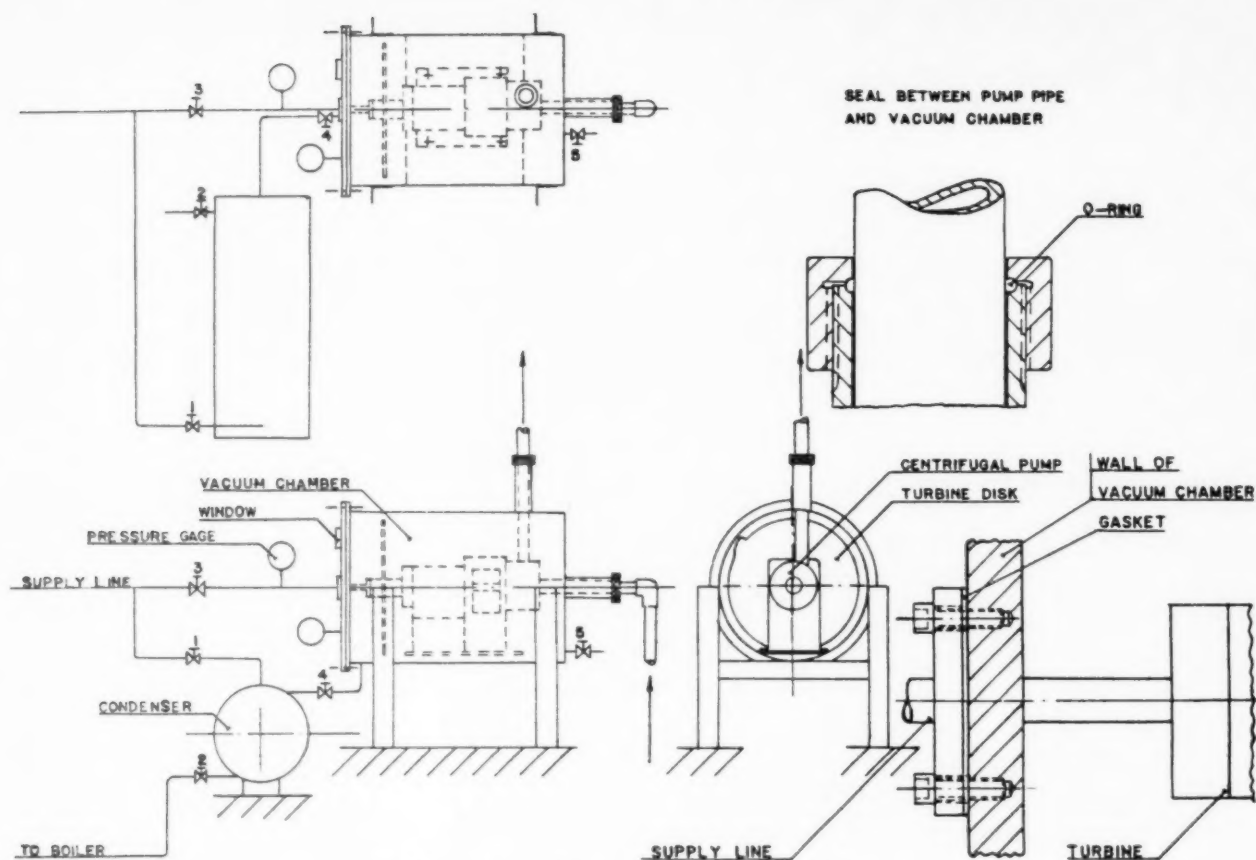
17

Fig. 4—Vacuum Chamber with Turbine and Pump
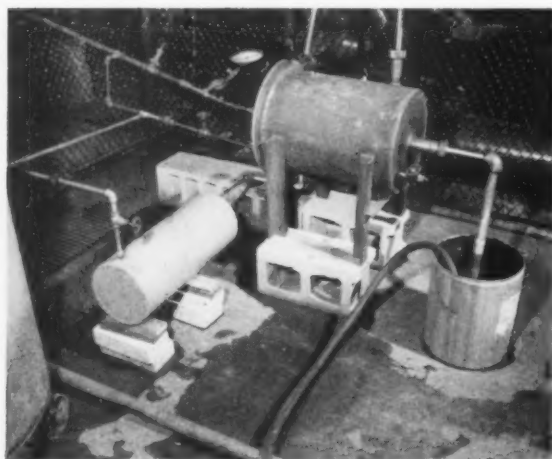
Fig. 5—Vacuum Chamber

psia and 281 F and expands through the turbine with a nozzle efficiency of 94.2 per cent to 10 psia and 176 F. The Freon which is in the superheated state after expansion has to be cooled to about 96 F before condensation takes place. The same amount of heat is added to the Freon as to the water.

The calculations show that there is a gain of about one per cent in maximum thermal brake efficiency when using Freon 113 instead of steam at 98 per cent quality, 50 psia and exhausting to 5 psia.

SUGGESTED IMPROVEMENTS AND APPLICATION

It is suggested that the vacuum chamber, turbine and pump be redesigned in aluminum as one complete unit to decrease weight and manufacturing cost.

The lip of the teflon seal should be thicker so that it will last longer and the steam inlet pipe should be made of aluminum to prevent corrosion of the surface in contact with the seal.

The vacuum chamber should be surrounded with water, which absorbs the heat that is released when the exhaust steam from the turbine condenses. The water jacket, surrounding the chamber, could be connected to a flash evaporator[3] where the warm water from the jacket would flash to vapor. The arrangement is shown diagrammatically in Figure 7.

The vacuum in the flash evaporator is obtained by bleeding water from the pump discharge line through a jet pump connected to the evaporator. When the desired pressure is reached in the evaporator, valves

Fig. 6—Reaction Turbine Operating under Vacuum Conditions and Driving Centrifugal Pump against a Head of 12 Feet.

Fig. 7—Suggested Arrangement of Solar Power Plant with Flash Evaporator.

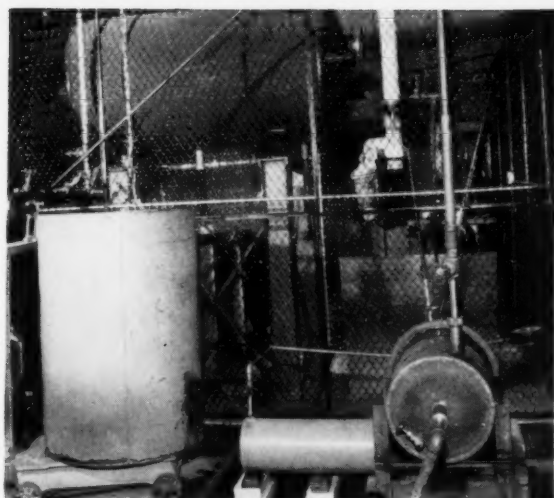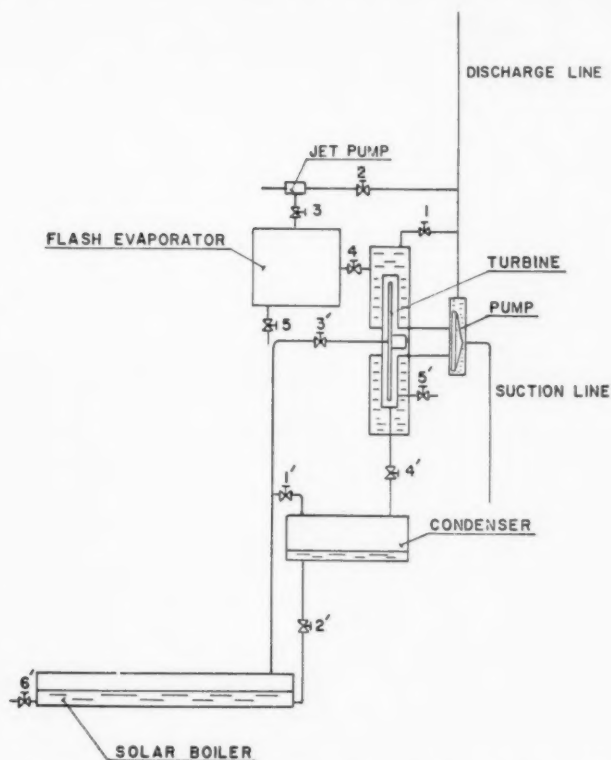(2) and (3) are closed, and valve (4) is opened to allow the water in the jacket to evaporate in the flash evaporator. After pressure equilibrium is reached between water jacket and evaporator, valve (4) is closed, and valve (1) is opened to fill the jacket with new water.

The vapor in the evaporator is condensed and the condensate is drained out by opening valves (3) and

(5). The turbine is operated in the same manner as described for Figure 4.

A solar power plant, designed to operate with a flash evaporator, would thus supply water for both household and irrigational purposes which is of great importance in areas where the water is polluted.

THE THERMO-ELECTRIC AND THERMIONIC GENERATORS

Either of these devices can be used to utilize solar energy. However, at the present time the cost of these generators is high, and they have to be handled with care. Both are high temperature devices with the thermo-electric generator operating at about 1100 F and the thermionic generator at about 2000 F.

The thermionic generator has not reached the development stage of the thermo-electric generator, but theoretically it appears that it should have a higher efficiency than the thermo-electric device, once the space charge between the cathode and anode has been eliminated.

The efficiency of the thermo-electric generator is about 6–7 per cent when operating between the temperature limits 1100 F and 80 F, while the theoretical efficiency of the thermionic generator is about 32 per cent when operating between the temperature limits 2066 F and 932 F and producing a current density of 10 amps per sq cm.

Both generators are high current and low voltage power devices. Therefore a large number of elements must be connected in series to obtain the usual voltage limits.

The thermo elements of the thermo-electric generator, which are sensitive to oxidation, have to be protected by means of a vacuum or an inert gas.

The operation of the thermo-electric and thermionic power devices by solar energy at the mentioned efficiencies requires concentration of the sun's rays by means of reflectors or lenses. The thermo-electric generator can be operated at a lower efficiency by using flat plate collectors, but collectors of the concentrating type are necessary to operate the thermionic generator.

CONCLUSIONS

The thermal brake efficiency of the reaction turbine is still low, about one per cent, when operating under vacuum conditions with steam at 50 psia, 98 per cent quality, and exhausting to a pressure of 5 psia. However, it has been shown that the turbine and vacuum chamber can be constructed by simple methods and of inexpensive material.

A closed system consisting of a flat plate type solar boiler, reaction turbine with vacuum chamber, pump, condenser, and flash evaporator should be designed

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and tested, since this combination may be a good solution to the problem of supplying the inhabitants in underdeveloped and arid regions with water for both irrigational and household purposes.

The thermo-electric and thermionic power devices may be useful for utilization of solar energy, but are not so rugged as the reaction turbine, and it would be difficult to repair or replace them in underdeveloped areas.

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Solar Furnace Determination of High-Temperature Absorption Coefficients

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Recent experiments have demonstrated that a solar furnace serves as an excellent tool for establishing heat absorption coefficients of materials at extremely high temperatures. An outline of the experiments with a naval brass sample (60.4% Cu, 39.6% Zn) illustrates the general method used. A sample was soaked at 1575°F and quenched in an ice bath so that the single-phase beta structure could be retained. This sample was then exposed in the furnace for 1.7 seconds and sectioned, polished, etched, and photographed. The *ASM Metals Handbook* gave the melting point at the exposed face, 1645°F, the temperature between the single-phase and two-phase regions near the exposed face, 1400°F, and the temperature between the two-phase region and the original structure, 675°F. The solar energy incident on the earth was calculated by calorimetry to be 1.9 calories/cm²/minute. The McAdams' equation is used for calculating the temperature profile of a semi-infinite solid by rapid heating for a short period. With a furnace efficiency of 30 per cent the absorption coefficient for brass is 0.17.

In order to determine the approximate temperature of a short-duration, high-temperature, gaseous environment through the study of phase changes in metals, it is necessary to establish antecedently, through experiment, the absorption coefficients of the metals involved for radiant energy at high temperatures. While tables of absorption coefficients are available in the 1000–1100°F range for many materials, tables up to 10,000°F are available only for a very select group of materials. In our study of gaseous environments we had to determine the absorption coefficients of certain materials independently, using a solar furnace. The method used in these experiments proved so effective that we believed extensive similar experiments would serve to establish rather complete lists of temperature coefficents for metals at extremely high temperatures.

The absorption coefficient of a material is normally established in a steady-state laboratory arrangement where a radiant energy source of some known temperature transmits energy to a specimen held at a constant temperature. The energy incident on the specimen and the energy absorbed by the specimen can be measured by calorimetry, and the absorption coefficient is simply the ratio of the absorbed energy to the incident energy.

The solar furnace available provided an excellent source for the necessary unvarying high-temperature radiant energy. A plasma jet would furnish higher temperatures, but it has convection in addition to radiation which is a disadvantage in this type of experiment. A solar furnace, having no forced air movement has negligible transfer of heat by convection. A parabolic mirror, five feet in diameter was modified to accommodate the necessary experimental equipment (Fig. 1). The mirror is supported on gimbal mounts which are driven by a constant-speed motor at the rate of one revolution per day. The declination can be set for any given day and the mirror will track the sun in its course. The specimens for the experiment are held in a half-inch drill chuck which can be moved readily in and out of the focal point of the mirror (Figs. 2 and 3). A two-leaf shutter in front of this focal point, operated by electrically-timed solenoids, permits timing of the exposures to one one-hundredth of a second.

Three metals—6061-T6 aluminum, cold rolled molybdenum, and naval brass (60.4% Cu, 39.6% Zn)—were exposed in the furnace for varying lengths of time, and the durations of exposure for each set of samples were varied sufficiently to cause a phase transformation in at least 80 per cent of the samples tested. The method used in the experiments can perhaps be best illustrated by explaining the experimental process in connection with a specific brass sample.

The brass sample was first soaked at 1575°F and then quenched in an ice bath so that the single-phase beta structure could be retained. The sample was exposed for 1.70 seconds in the solar furnace and then, using standard metallographic techniques, was sectioned,
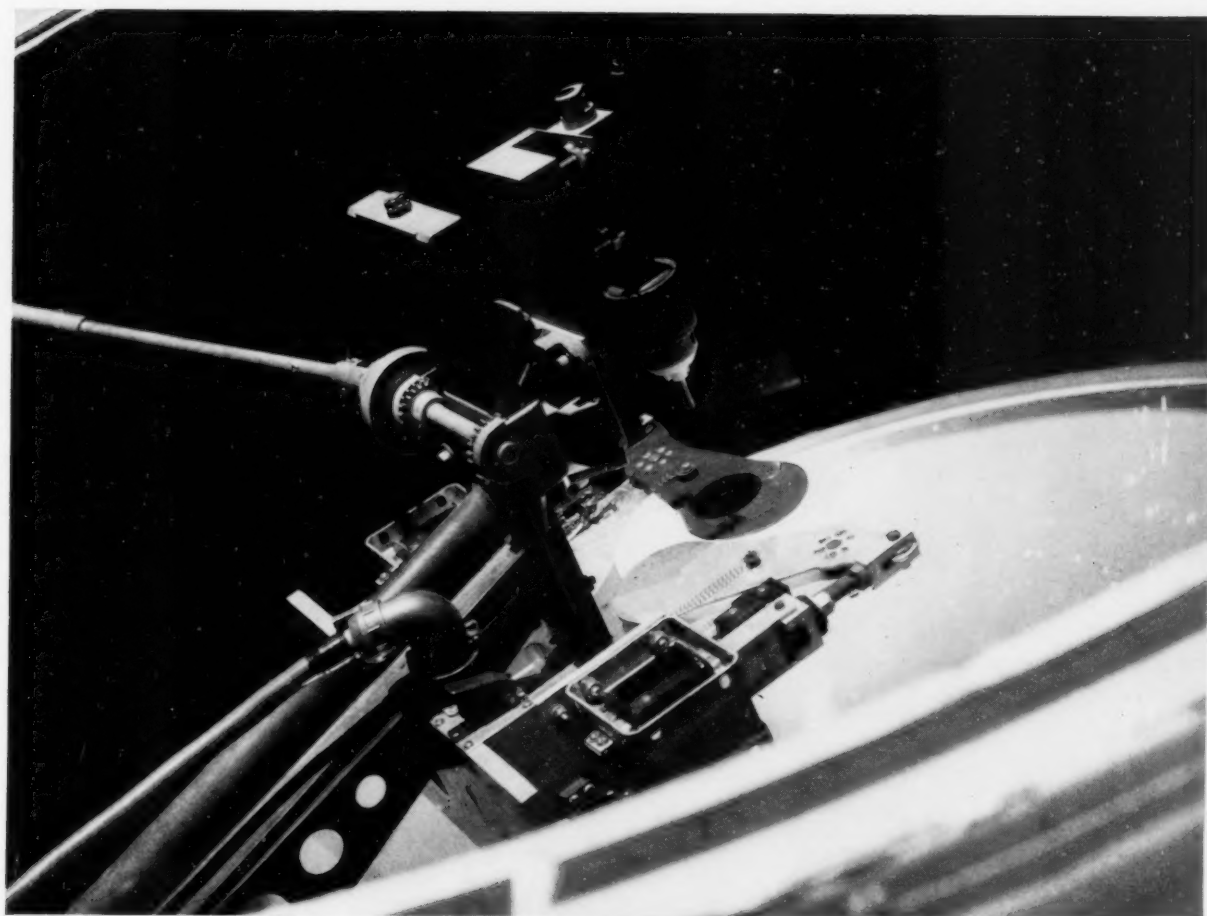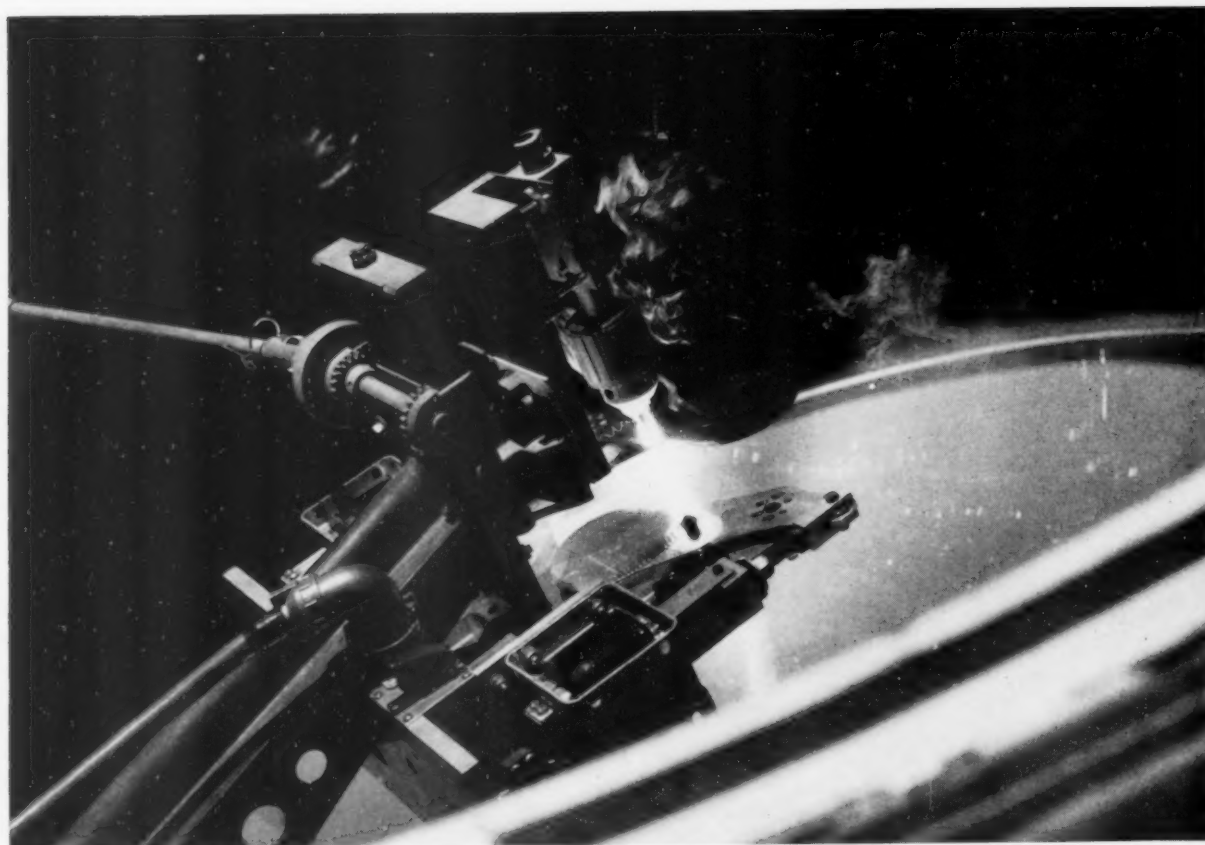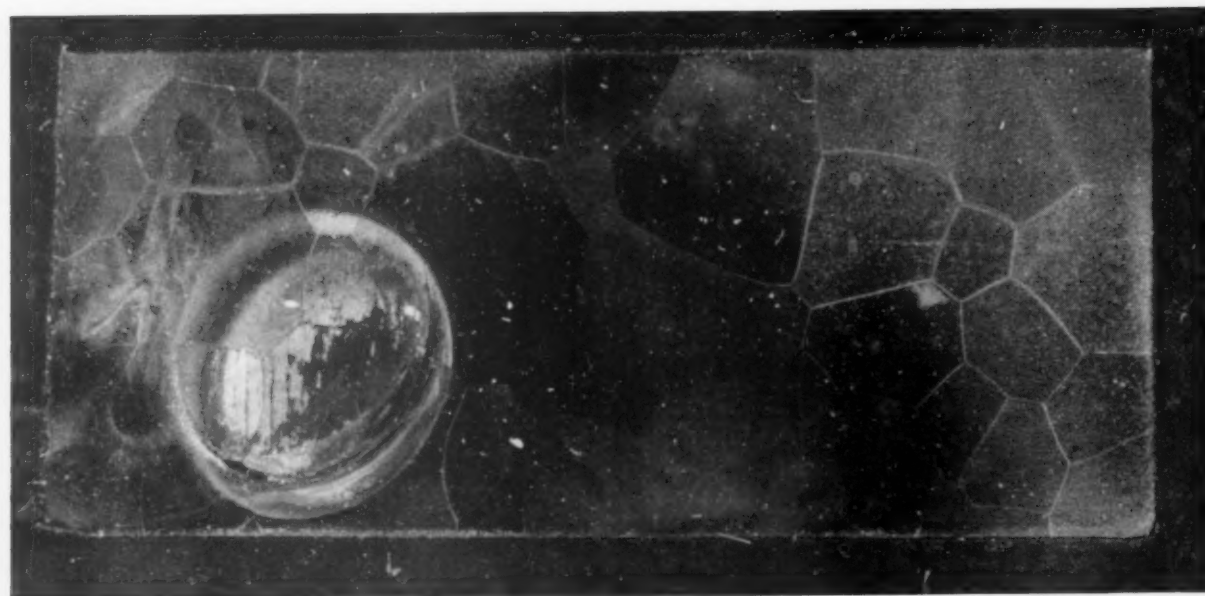
Fig. 1

Fig. 2

FIG. 3

FIG. 4—Metallographic Section of an Exposed Brass Sample with the Exposed Face to the Right

polished, and etched. After it had been etched, the specimen was photographed on a Bausch and Lomb metallograph in order to measure the distance from the exposed face of the sample at which certain temperatures occurred (Figs. 4, 5, and 6).

The *ASM Metals Handbook* supplied important reference information: (1) the melting point at the exposed face, 1645°F, (2) the temperature between the single-phase and two-phase regions near the exposed face for this composition, 1400° F, and (3) the temperature between the two-phase region and the original structure, 675°F. Calorimetric calculations indicated that the solar energy incident on the earth at 5400 feet (the elevation at Sandia) was 1.94 calories/cm²/minute. This value was so close to the 1.92 calories/cm²/minute given in *The Handbook of Chem-*

istry and Physics that calorimetric measurement was not pursued further, especially since the accuracy demanded for this experiment was not extremely high. McAdams supplies the equations necessary for calculating the temperature profile of a semi-infinite solid from the data obtained in rapidly heating a relatively thick body for a short time (the conditions present in the solar furnace exposure):

$$Y = \frac{2}{\sqrt{\pi}} \int_0^z e^{-z^2} \cdot dZ$$

$$Y = \frac{ta - t}{ta - tb} \qquad Z = \frac{x}{2\sqrt{\beta\theta}}$$

Y = the unaccomplished temperature change
ta = temperature of the surroundings in °F
tb = uniform base temperature in °F
t = temperature at point x in °F
x = distance from the exposed surface in feet
β = thermal diffusivity in ft²/hr
θ = time in hours

The calculated profile for the brass sample is given in Fig. 7. The energy absorbed by the specimen is calculated by integrating the area under the curve with the known average specific heat of the metal. The curve (or the equation) gives the value for the temperature in °F at any distance, x, from the exposed face of the sample.

According to *The Handbook of Chemistry and Physics*, the reflection of a solar spectrum by polished stellite, which is used as the reflecting surface in this furnace, is between 30 and 40 percent efficient. Since a small portion of the solar furnace mirror is obscured by the mounting for the sample holder, the efficiency was
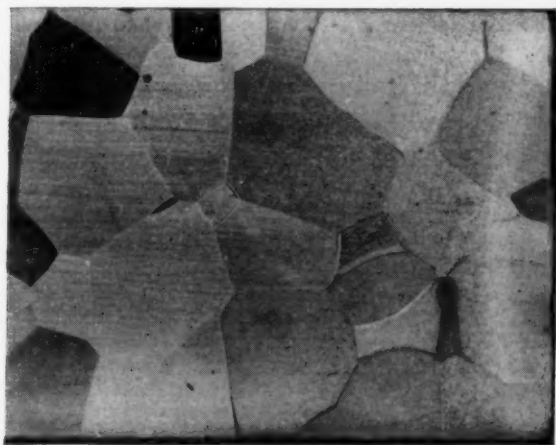

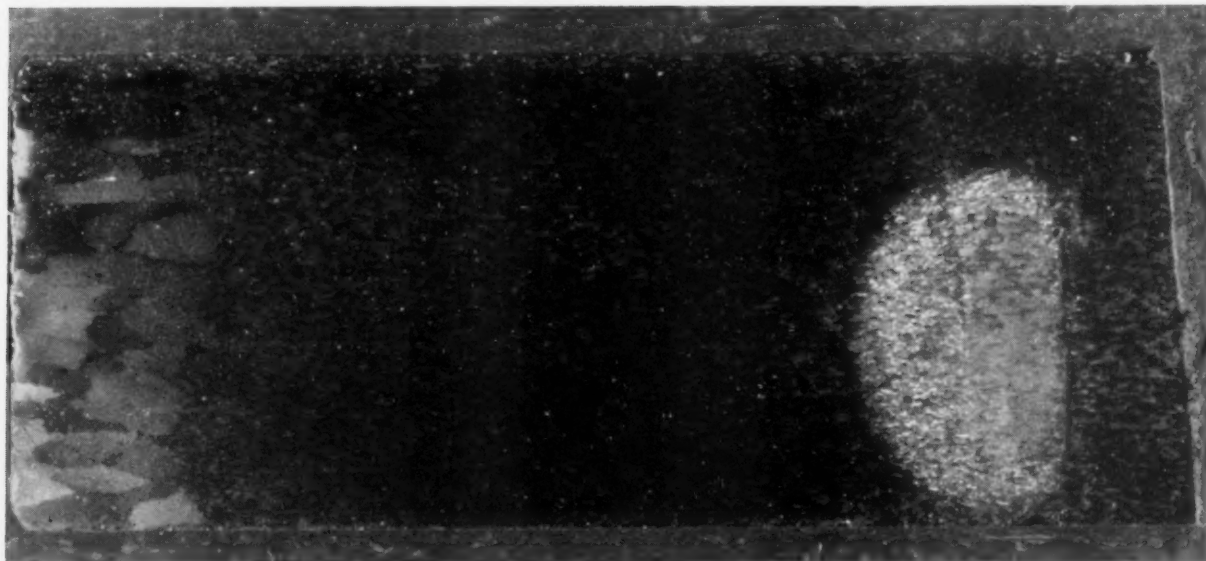Fig. 5—Metallographic Section of an Exposed Brass Sample with the Exposed Face to the Right

Fig. 6—Metallographic Section of an Exposed Molybdenum Sample with the Exposed Face to the Left
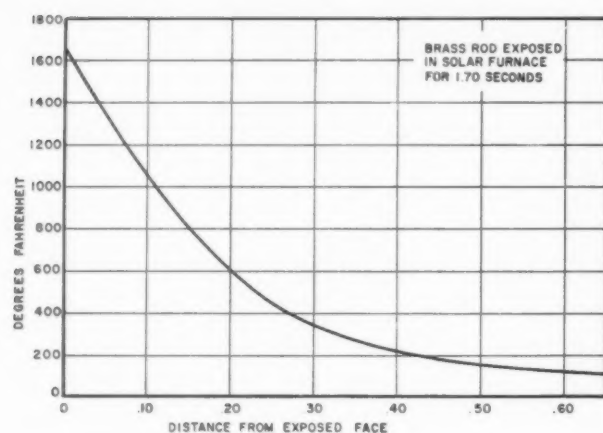
CALCULATED TEMPERATURE PROFILE

BRASS ROD EXPOSED
IN SOLAR FURNACE
FOR 1.70 SECONDS

Figure 7

Fig. 7

Table I—Absorption Coefficients

Metal	Coefficients	Source Temperature
6061-T6 aluminum	0.05	approximately 7000°F
Cold rolled molybdenum	0.27	approximately 7000°F
Naval brass	0.17	approximately 7000°F

taken at the minimum of 30 per cent. Since the energy reflected by the furnace was concentrated in an area smaller than the exposed face of the specimen, it was certain that at least 30 per cent of the energy incident on the mirror was also incident on the sample.

The energy absorbed by the sample during the 1.70 second exposure was arrived at by the summation of $V\rho c_p \Delta t$, utilizing the temperature profile for values of V and t. The terms in the summation are volume, density, specific heat, and temperature respectively. The absorption coefficient is the ratio of the absorbed energy to incident energy and is noted as α in heat transfer equations.

$$\alpha = \frac{\text{Energy absorbed}}{\text{Energy incident}}$$

$$= \frac{V\rho c_p \Delta t \text{ (From Fig. 7)}}{\text{Area of mirror} \cdot \text{solar constant} \cdot \text{efficiency} \cdot \text{time}} \cdot$$

$$\alpha = \frac{0.203 \text{ BTU}}{\frac{1.94}{60} \cdot 13{,}272 \text{ Btu/hr/ft}^2 \cdot (2.5)^2 \pi \text{ ft}^2 \cdot \frac{1.70 \text{ sec}}{3600 \text{ sec/hr}} \cdot 30\%}$$

$\alpha = 0.17$, the effective absorption coefficient for the conditions in the solar furnace.

Using a solar furnace comparable in type and size to that used at Sandia, Arthur D. Little, Inc., of Cambridge, Massachusetts, obtained temperatures up to 6300°F. Using the absorption coefficient obtained from the previously mentioned brass sample, a temperature of 7300°F in the solar furnace at Sandia was indicated. The approximate agreement of the two temperatures justified the use of the absorption coefficients obtained in the furnace for further calculations. Table I lists the values obtained for the three metals used in these experiments.

The solar furnace has thus proved to be an extremely useful and accurate tool for determining absorption coefficients for radiant energy transfer. The incident energy could undoubtedly be determined more accurately with more thorough calorimetric measurements. Further work along these lines would yield far more extensive data on absorption coefficients at high temperatures on materials which are not availabe in present tables.

REFERENCE

1. W. H. McAdams. *Heat Transmission*, 3rd Edition, McGraw-Hill Book Co., Inc., New York, 1954.

Solar Reflectance Integrating Sphere

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An inexpensive integrating sphere for the direct determination of the reflectance of materials irradiated by solar energy transmitted through the atmosphere of the earth is described. Reflectance and transmittance measurements of various metals, cloths, and filters are reported and are compared to spectral and total measurements made with other instruments.

INTRODUCTION

Solar radiation is an important part of the thermal environment of many industrial, agricultural, and architectural systems. Values of the solar reflectance are thus required for thermal design and analysis of such systems.

The total solar reflectance is defined by the ratio

$$r = \int_0^\infty r_\lambda S_\lambda \, d\lambda \Big/ \int_0^\infty S_\lambda \, d\lambda = R/S$$

where S is the total solar irradiation striking the surface, R is the total energy reflected from the surface in all directions, r_λ is the spectral reflectance, and S_λ is the spectral solar irradiation. In general this quantity depends upon the angle of incidence of the solar irradiation. In this paper consideration is limited to near-normal angles of incidence.

Measurement of the solar reflectance is commonly accomplished by measuring spectral reflectances with a spectrophotometer and integrating the spectral data. Such instruments are relatively expensive, generally costing $10,000 to $20,000. Direct total measurements have been made with a Coblentz sphere[2, 10] but such instruments which contain metal mirrors are likely to give somewhat erroneous values due to the characteristic decrease of reflectivity of metals in the short-wave region of the solar spectrum. In addition, the Coblentz sphere yields somewhat erroneous values for diffuse materials due to non-uniform angular response of the detector, optical aberrations, and interreflections.[3]

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The instrument described in this paper permits rapid direct measurement of the reflectance of materials irradiated with solar energy transmitted through the atmosphere and is relatively inexpensive to construct. It has been used to measure the solar reflectances of cloths under the sponsorship of the U.S. Army Quartermaster Corps contract number DA-19-129-QM-149.[1] An evaluation of the performance of the instrument and recommendations for improvements as a result of subsequent experience are included; this evaluation was supported in part by NSF Grant G 9505.

Description of Apparatus

The apparatus is shown in Fig. 1. It consists of an equatorially mounted integrating sphere with a thermopile detector. Solar energy may be admitted directly into the sphere without the use of auxiliary optics.

Two spun copper hemispheres 12 in. in diameter and 0.06 in. thick form the integrating sphere. The interior surface is coated with three coats of titanium dioxide in a lacquer vehicle and a 0.03 in. thick layer of magnesium oxide. Since a total energy detector is used, the exterior surface is insulated with a $\frac{1}{2}$ in. thick layer of asbestos cement to reduce drift.

A 1.19 in. aperture in the sphere forms the entrance port. A holder for the shutter plate, stop plate, and sample plate are provided at this entrance port. Across the sphere are located two sample holders, one on each side of the thermopile detector.

A detailed view of the detector is presented in Fig. 2. Two 0.03 in. thick bakelite forms are glued with Duco cement on the sides of a copper block. A silver-constantan thermopile[7] of approximately 150 junctions on either side of the copper block is formed by 0.002 in. constantan wire silver-plated on one-half. Receiver strips of 0.125 in. wide aluminum foil painted with Boysen Flat Black enamel on the exposed surface cover the lines of junctions. Thermal and mechanical contact to the wire is made by lacquer while the shellac on the back of the strip prevents electrical shorting. Two mounting screws at each end of the copper block hold the detector in place in the detector housing.

A sample holder is illustrated in detail in Fig. 3. The sample is held in place with a 0.06 in. thick, 1.38 in. inner diameter retaining ring. The face of the ring
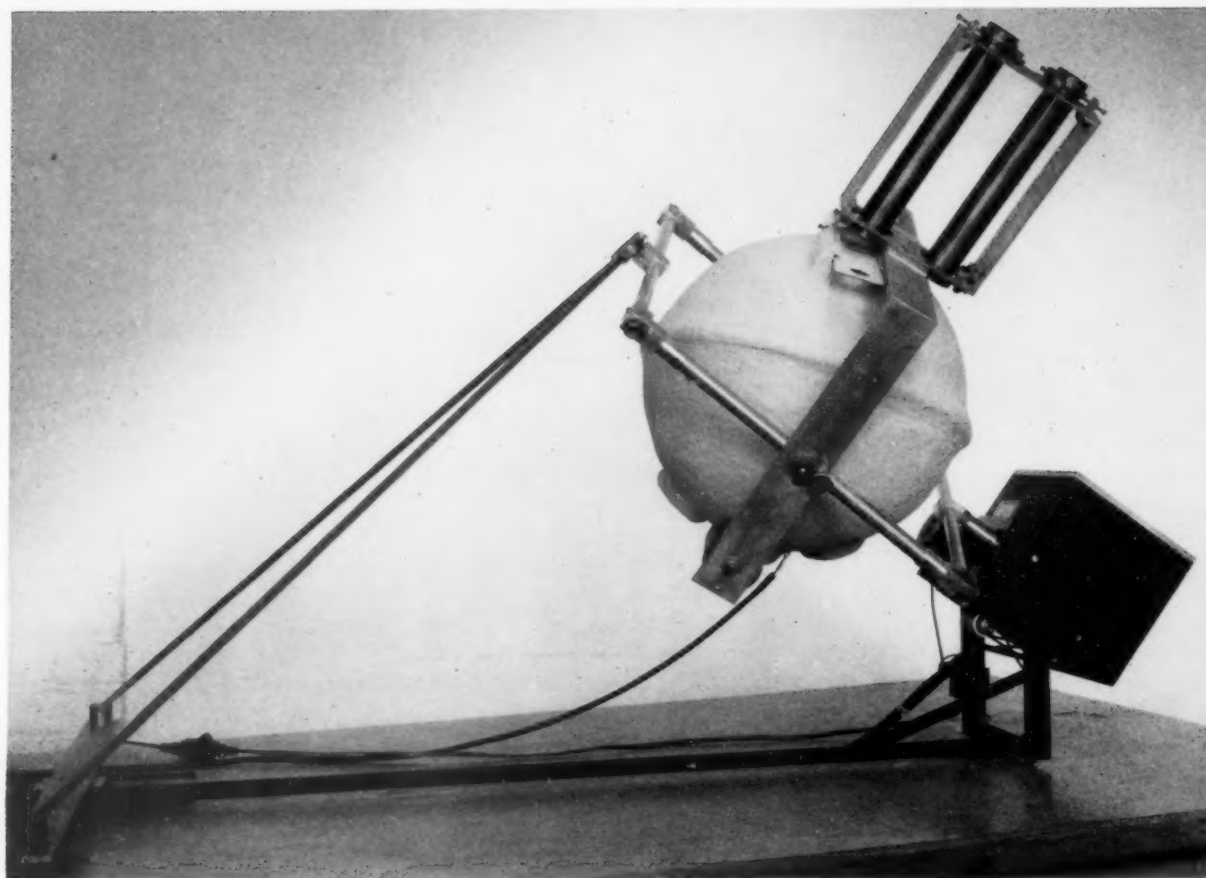
Fig. 1—Solar Reflectance Integrating Sphere

is coated in the same fashion as the sphere walls. A spacer between the face of the holder and the sample (or samples) raises the outer sample face to the level of the integrating sphere surface when the holder is screwed into place in the socket on the sphere.

The relative positions of the sample holders, entrance port, and thermopile detector are shown in Fig. 4. As indicated in this figure, two 1.25 in.-diameter, 9 in.-long tubes painted black on the interior serve to mask the entrance port from sky radiation. These tubes are located on a yoke in which the integrating sphere may be rotated (see Fig. 1). Rotation of the sphere in the yoke makes it possible to direct solar energy through one or the other of the tubes onto the desired sample holder as indicated in Fig. 4. The solar energy strikes the sample 15° from the normal in either position. Each position is fixed by adjustable mechanical stops against which the sphere is rotated and a thumbscrew which is tightened to hold the sphere in place.

An equatorial mounting contains the yoke together with the sphere and tubes as shown in Fig. 1. This mounting is driven one revolution per day by a synchronous motor acting through reducing gears. The yoke holding the sphere and tubes may be rotated in a plane containing the axis of the equatorial mounting in order to adjust for the declination of the sun.

A 2 millivolt recording potentiometer with a $\frac{1}{2}$ second response time is used for measurement of the thermopile output voltage.

OPERATING PROCEDURE

Preliminary Steps

Setting up the apparatus for measurements is accomplished as follows:

(1) The instrument is placed on a table in an open area on a clear day, aligned in a north-south direction and leveled so that the axis of rotation of the equatorial mount is parallel to the axis of the earth. The drive motor is started, and the entrance tube is pointed towards the sun.

(2) Alignment is checked by observing with a small dental mirror the location on the reference sample of the area illuminated by the sun. The alignment is then further checked by similarly observing the illuminated area on the test samples in the second sample holder.

(3) Steadiness of the recorded signal with the sphere

BARE CONSTANTAN WIRE .002 INCHES DIAM.

RECEIVER STRIP

1/2

1 1/2

SILVER PLATED WIRE

MOUNTING SCREWS

BAKELITE FORM .031 INCHES THICK

5/16

1/8

COPPER BLOCK

RADIUS OF CURVATURE OF SPHERE
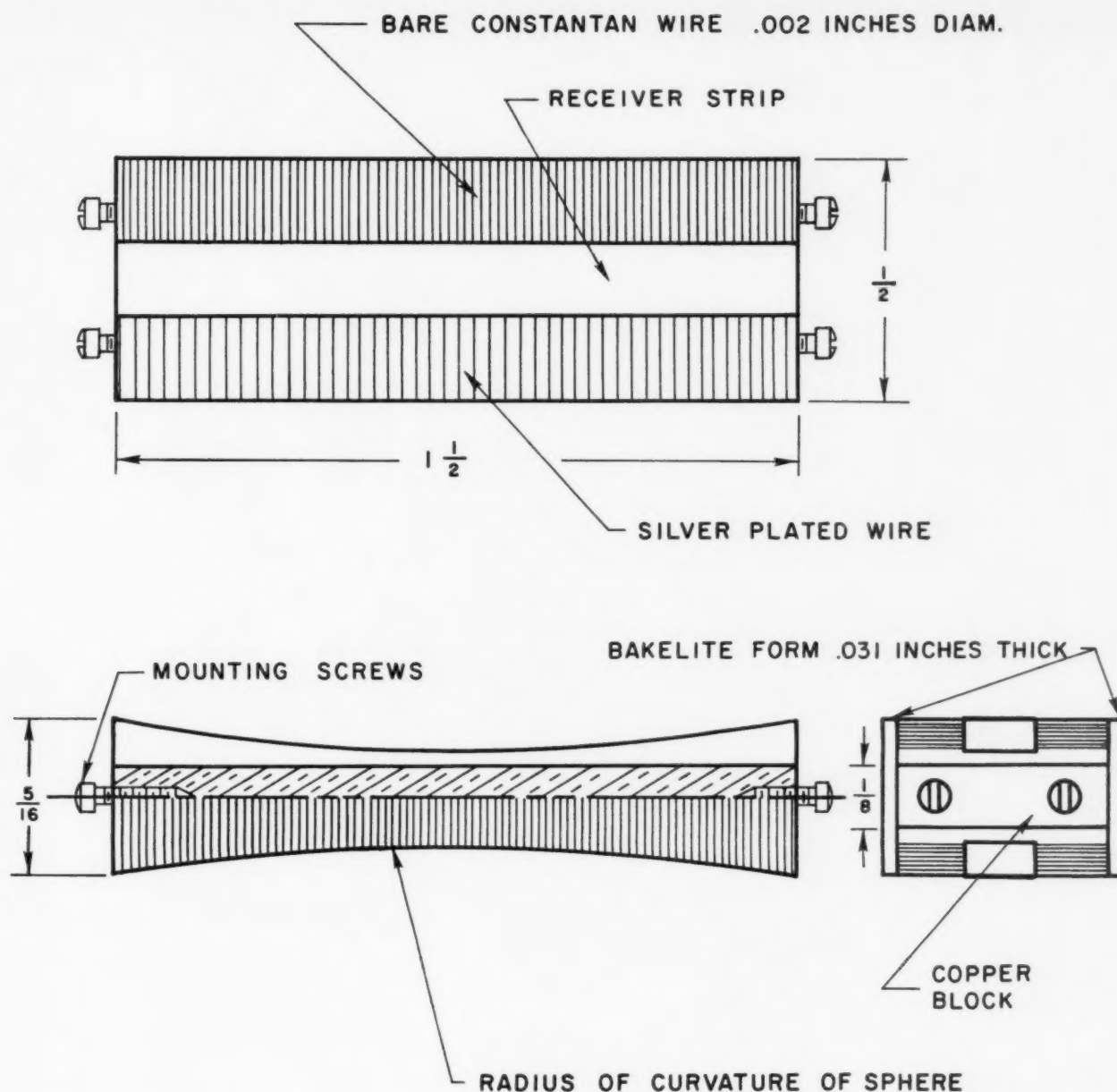
Fig. 2—Details of Thermopile Detector

in the reference sample position is observed to determine that no atmospheric phenomena are introducing random errors.

Reflectance Measurements

The procedure for reflectance measurements is as follows:

(1) The shutter is opened for one minute to allow solar energy to fall on the reference sample.
(2) The shutter is closed one minute.
(3) The sphere is rotated, and the shutter is opened one minute to allow sunlight to strike the unknown sample.

(4) The shutter is closed one minute.
(5) The sphere is rotated back to the reference position, and the shutter is opened for one minute.
(6) Steps two through five are repeated until several consistent values are obtained.

Transmittance Measurements

The transmittance of non-diffusing materials are measured with the procedure listed below. If the integrating sphere is fitted with a mask, as will be discussed in another section, the above procedure will also give valid results for translucent materials with steps 3 and 5 changed as follows:

VOL.
4
1960
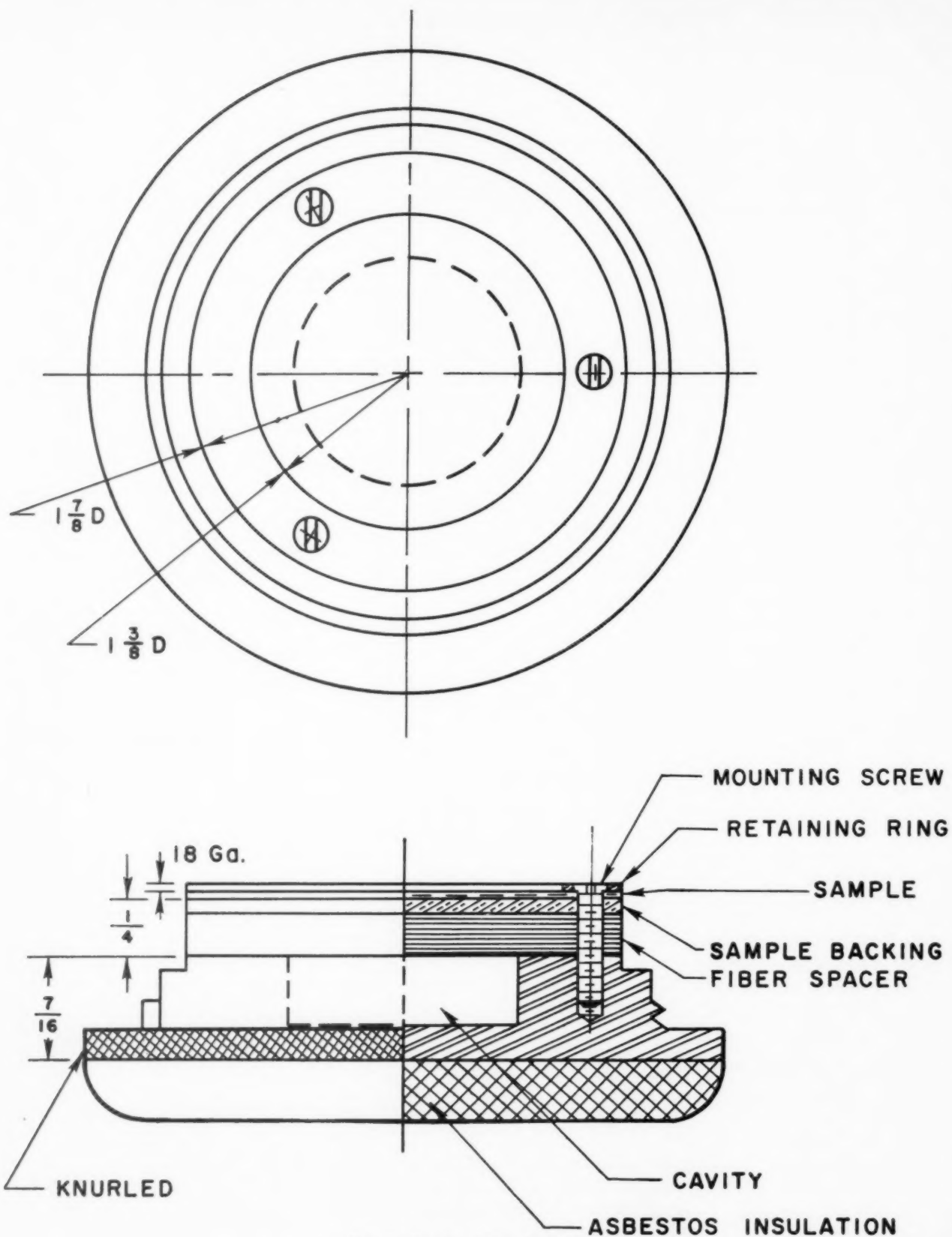
FIG. 3—Details of Sample Holder

30

SUNRAY →

SHUTTER

SOLARIMETER
PIVOTED TO
UNKNOWN SAMPLE
POSITION

INTEGRATING SPHERE

PIVOT AXIS

STANDARD SAMPLE
HOLDER

UNKNOWN SAMPLE
HOLDER FOR
REFLECTIVITY TESTS

THERMOPILE DETECTOR

SUNRAY

SOLARIMETER
PIVOTED TO
STANDARD SAMPLE
POSITION

SAMPLE FOR
TRANSMISSIVITY TESTS

SHUTTER

INTEGRATING SPHERE

STANDARD
SAMPLE HOLDER

THERMOPILE DETECTOR
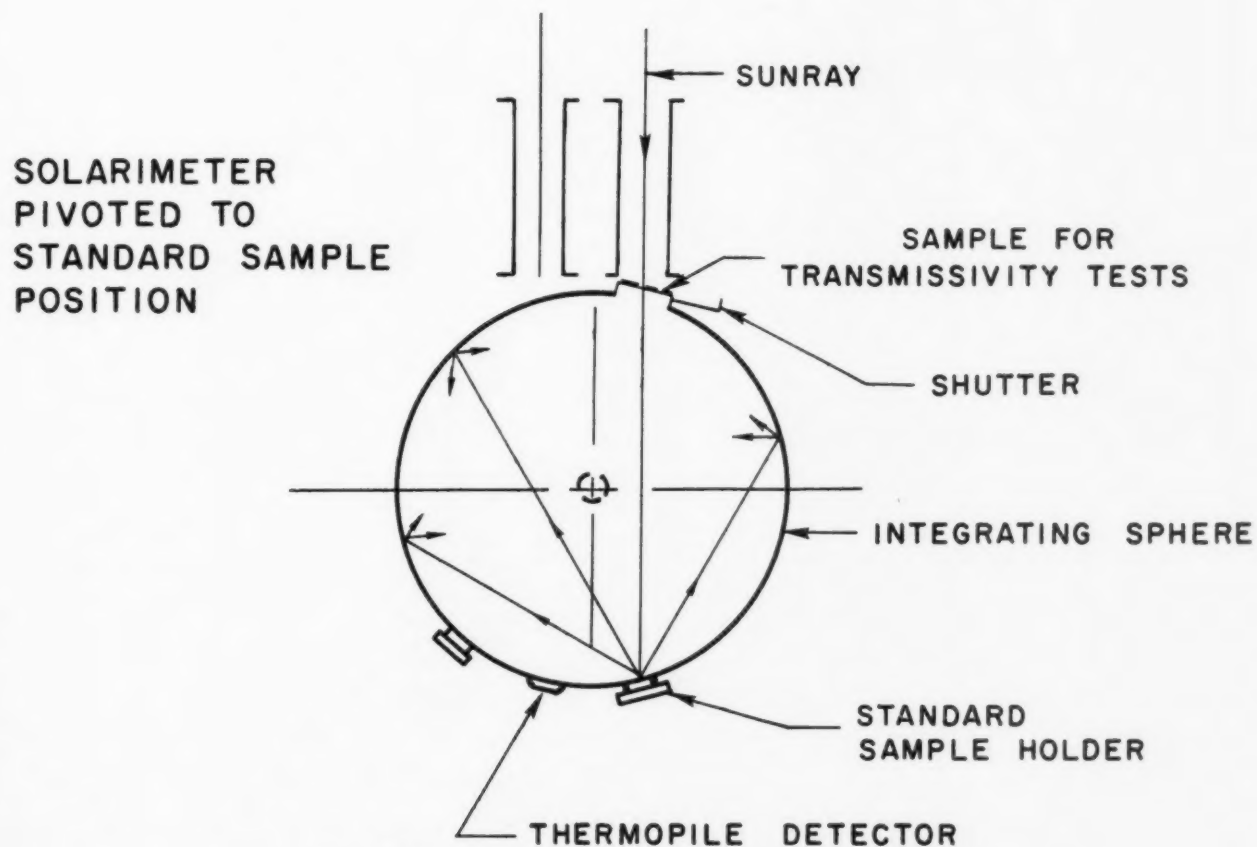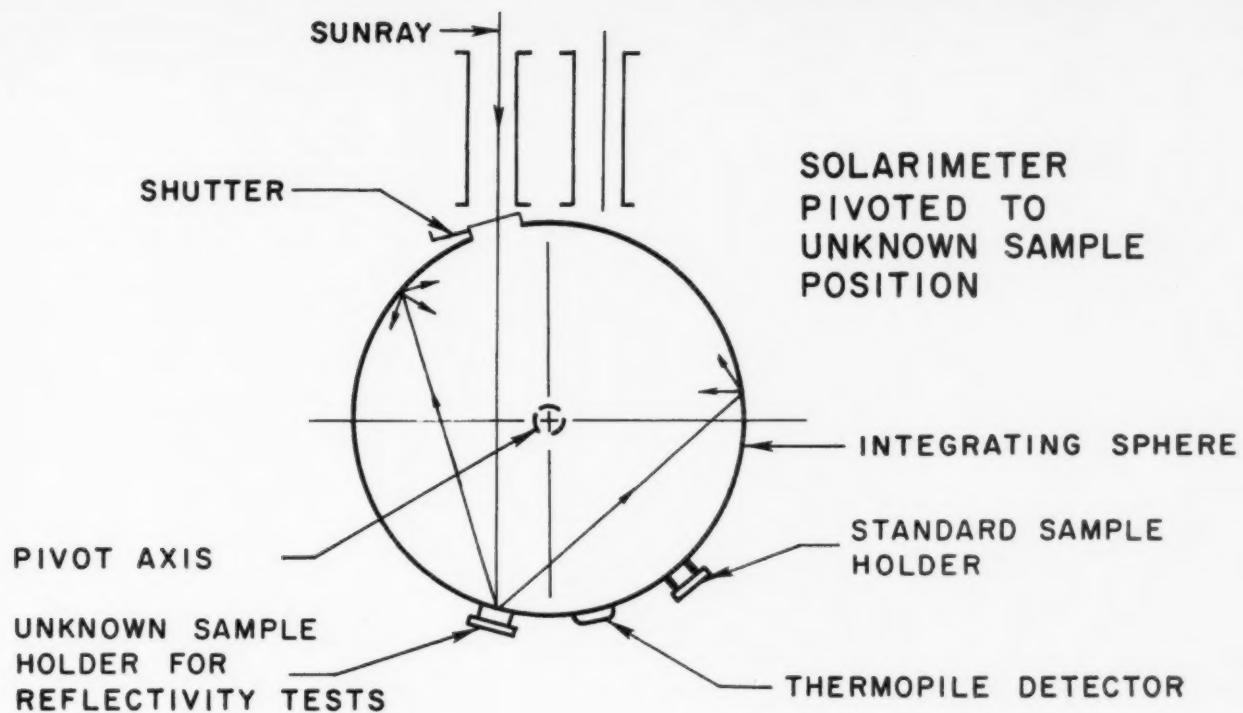
FIG. 4—Schematic Diagram of Solar Reflectance Integrating Sphere

31
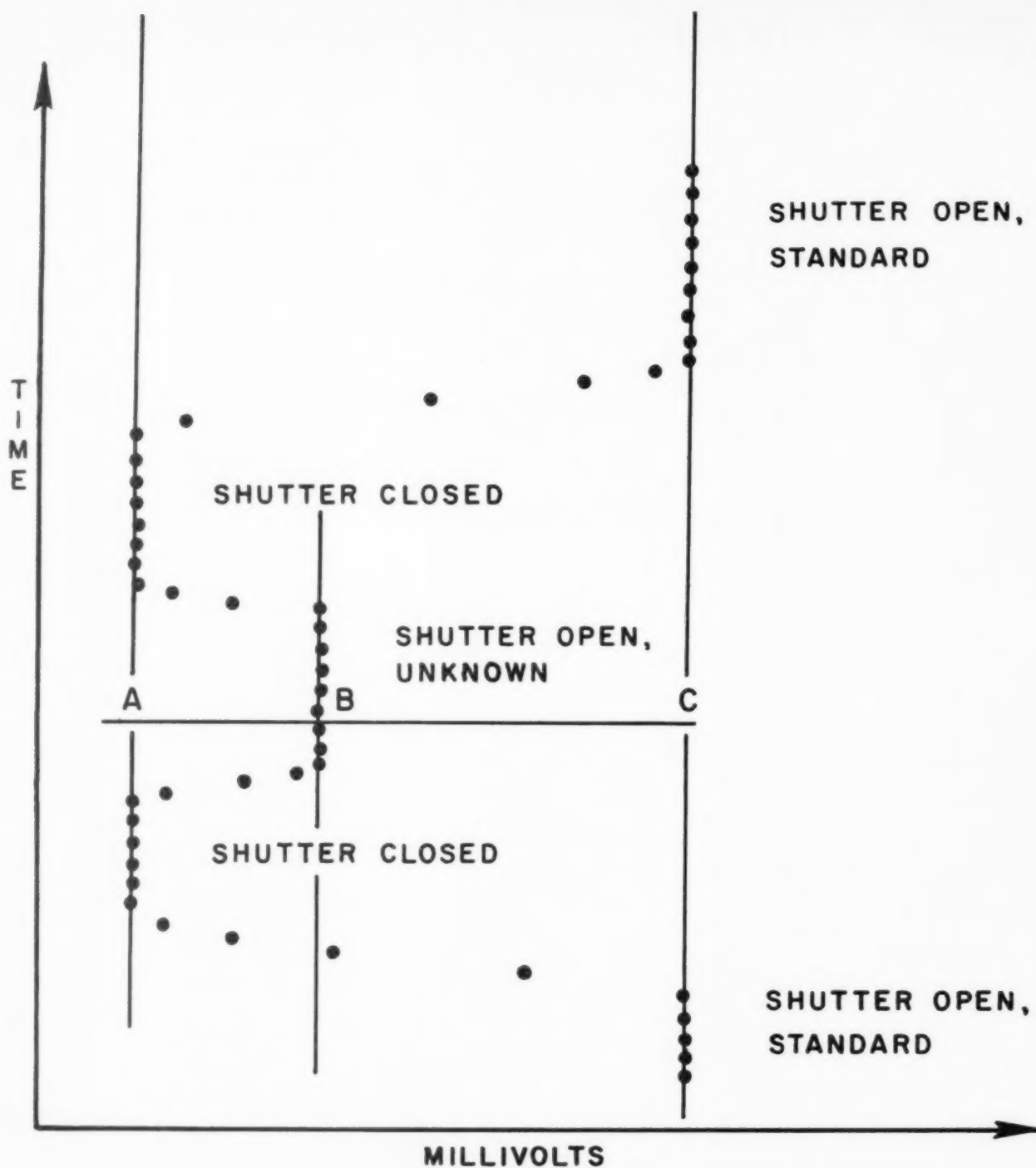
FIG. 5—Typical Data Curve

(3) The sample is inserted under the stop at the entrance port of the sphere, and the shutter is opened one minute.

(5) The sample is removed and the shutter opened one minute.

Computation of Results

Lines are drawn through the reference and shutter readings on the recorded data as shown in Fig. 5. Measurements of the distance $\overline{AB}$ and $\overline{AC}$ in Fig. 5 are made with a ruler to 0.01 in. The ratio $\overline{AB}/\ \overline{CA}$

TABLE I—Comparison of Reflectances of Metals Obtained from Solar Reflectance Integrating Sphere and from Integration of Spectral Data

Metal Sample	Reflectance		Discrep- ancy
	Solar Reflectivity Meter	Integration of Special Data	
24 ST 81 Aluminum Alloy Sulfuric Acid Anodize Coating	.56	.53	+ .03
24 ST 81 Alclad Chromic Acid Anodize Coating	.56	.60	− .04
24 ST 81 Chem-milled Sulfuric Acid Anodize Coating	.64	.57	+ .07
24 ST 81 Aluminum Alloy Black Chromic Acid Anodize Coating	.31	.29	+ .02
24 ST 81 Alclad Sulfuric Acid Anodize Coating	.69	.63	+ .06
24 ST 81 Alclad Black Chromic Acid Anodize Coating	.31	.33	− .02
24 ST 81 Aluminum Alloy Chromic Acid Anodize Coating	.28	.30	− .02
Titanium	.37	.36	+ .01

gives the transmittance in the case of transmission tests or the ratio of the reflectance of the unknown to that of the reference sample in the case of reflection tests. Distance $\overline{AC}$ is generally 3 to 3.5 in., that is, the thermopile output is usually 0.6 to 0.7 millivolts.

In the case of partially transparent materials such as cloth, reflectance measurements are made with white paint and black paint backgrounds which have measured reflectances of r_1 and r_2 respectively. This procedure is necessary to account for energy transmitted through the material and reflected by the background. The true reflectance of the material tested is taken as

$$\rho = \rho_2 - (r_2/r_1)(1 - r_1\rho_2)(\rho_1 - \rho_2)$$

where ρ_1 and ρ_2 are the observed reflectances of the material with the white and black backgrounds respectively. Since backgrounds with measured values $r_2 = 0.10$ and $r_1 = 0.82$ are used, the correction term is small.

RESULTS

Reflectance

The results of reflectance measurements of metals with various surface coatings are compared in Table I with values obtained from integration of spectral measurements made with a General Electric spectrophotometer in the 0.4 to 1 micron range and a Gier-Dunkle absolute reflectometer[3, 4] in the infrared. The spectral data are shown in Fig. 6. For the purposes of integration the solar spectrum was approximated from the summary of Moon.[13] The spectrophotometer results are relative to magnesium carbonate and were used uncorrected in the integration, since some doubt remains as to the correct absolute spectral reflectance of $MgCO_3$.[3] In any case the correction would probably

be less than two percent. The direct measurements of solar reflectance are corrected for a reference sample reflectance of 0.95.

Results of reflectance measurements for various cloths are compared in Table II with integrated values obtained from spectral data given in Fig. 7. Measurements with white and black backgrounds under the cloth permitted a small correction to be made for the energy transmitted through the cloth and reflected from the black background. Spectral data were again determined with a General Electric spectrophotometer and a Gier-Dunkle absolute reflectometer.

Transmittance

Transmittance measurements of various non-diffusing glasses are compared with measurements made with the Gier-Dunkle directional radiometer[9] in Table III.
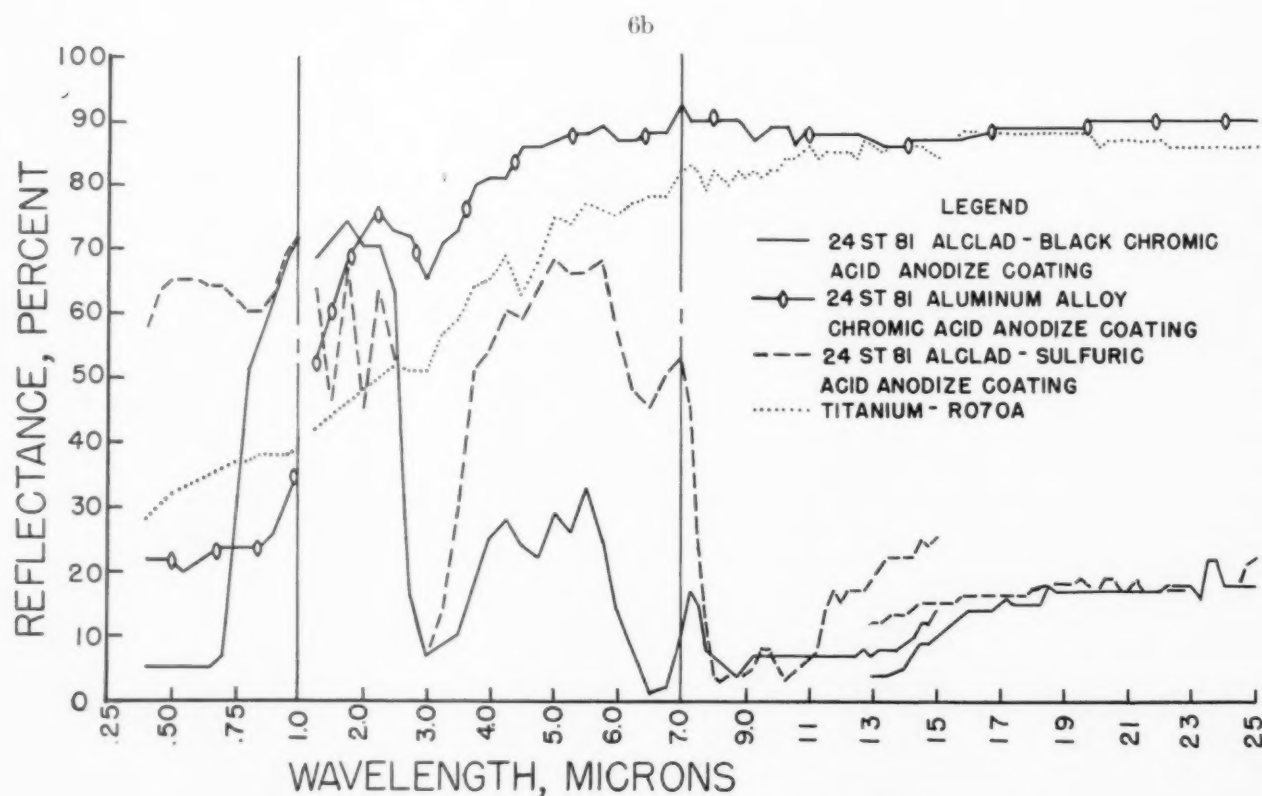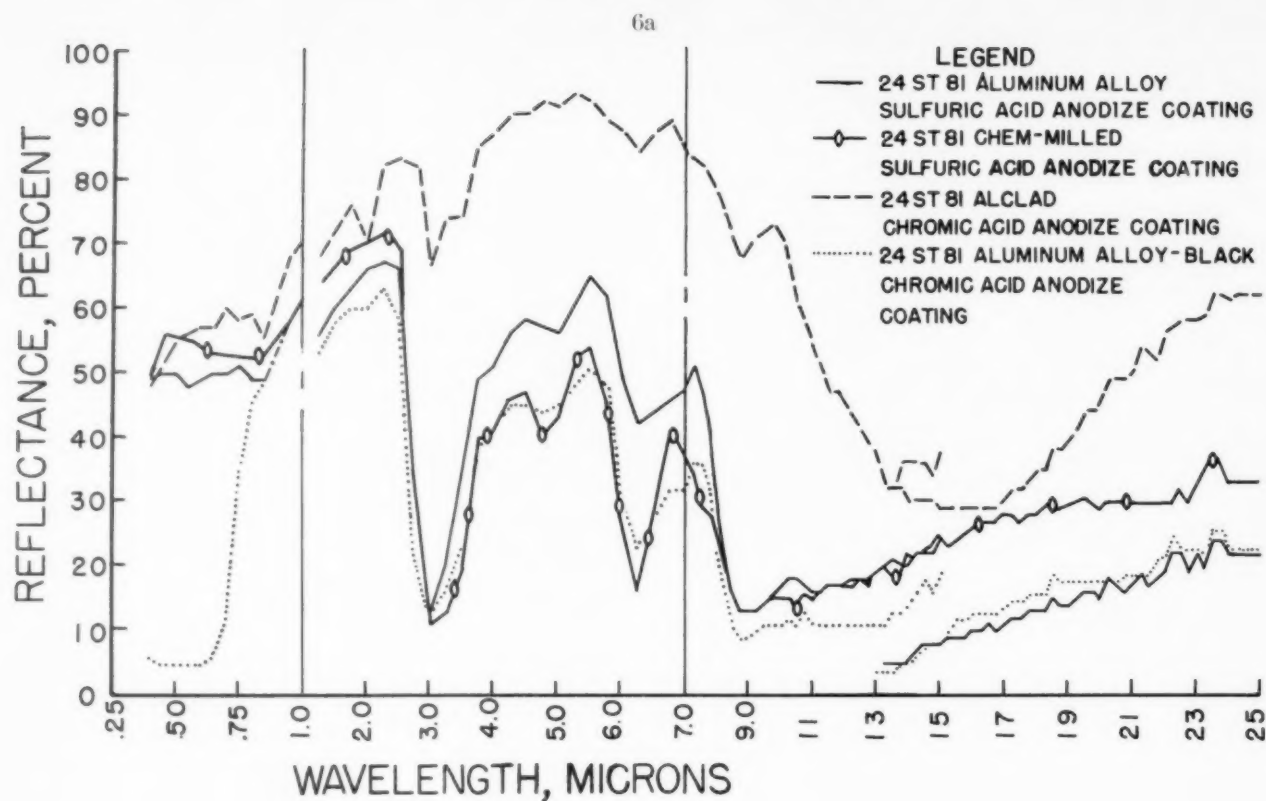
DISCUSSION

Reflectance of Reference Sample

Reference samples were prepared in the same manner as the sphere walls. A coating of magnesium oxide 0.03 to 0.04 in. thick was smoked onto polished copper which had been painted with three coats of titanium dioxide pigment in a lacquer vehicle. Reflectance measurements of such a layer of magnesium oxide on black paint and polished aluminum made with the absolute reflectometer[5] indicates such a surface has a reflectance of about 0.92 between 1 and 2 microns. Middleton and Sanders[12, 14] obtained spectral reflectances of magnesium oxide ranging from 0.94 to 0.98 between 0.24 and 0.85 microns, the value depending upon the thickness. The spectral reflectance of a given sample varies only about 0.02 in the range from 0.25 to 0.85 microns. In the light of these measurements, the spectral reflectance of the reference sample is probably about 0.95 in the visible and about 0.92 in the near infrared. The solar reflectance of the reference sample is thus very likely 0.95 ± 0.03.

Performance

The deviations of the values of reflectance and transmittance measured with the solar integrating sphere from those obtained from integration of spectral data or from measurement with the directional radiometer show a definite trend. Measurements with the solar integrating sphere for samples which transmit more energy in the visible than in the infrared, such as the *E. Z. Eye* tinted glass, the heat absorbing glass, and the plexiglasses, are higher than the measurements with the directional radiometer. Conversely, measurements with the integrating sphere for samples which

6a

LEGEND
— 24 ST 8I ALUMINUM ALLOY
  SULFURIC ACID ANODIZE COATING
—◇— 24 ST 8I CHEM-MILLED
  SULFURIC ACID ANODIZE COATING
--- 24ST 8I ALCLAD
  CHROMIC ACID ANODIZE COATING
····· 24 ST 8I ALUMINUM ALLOY-BLACK
  CHROMIC ACID ANODIZE
  COATING

REFLECTANCE, PERCENT

WAVELENGTH, MICRONS

6b

LEGEND
— 24 ST 8I ALCLAD-BLACK CHROMIC
  ACID ANODIZE COATING
—◇— 24 ST 8I ALUMINUM ALLOY
  CHROMIC ACID ANODIZE COATING
--- 24 ST 8I ALCLAD - SULFURIC
  ACID ANODIZE COATING
····· TITANIUM - RO7OA

REFLECTANCE, PERCENT

WAVELENGTH, MICRONS

FIGS. 6a–6b—Spectral Reflectances of Metals with Various Surface Coatings

34

Table II—Comparison of Integrated Solar Reflectance from Spectral Data with Solar Reflectance Integrating Sphere Results

Cloth	Reflectance		Discrep-ancy
	Solar Reflectivity Meter	Integrated from Spectral Data	
Cotton Poplin Green RPS-1 5 oz/yd (No. 1)	.26	.22	+.04
Cotton Knit Undyed 3 oz/yd (No. 2)	.60	.62	−.02
Cotton Sateen Olive Drab (06107) 9 oz/yd (No. 3)	.19	.18	+.01
Mohair Double Face Frieze Undyed 16 oz/yd (No. 5)	.63	.56	+.07
85% Wool 15% Nylon Shirting Olive Drab (06108) 10.3 oz/yd (No. 7)	.20	.18	+.02
50% Wool 50% Cotton Knit Undyed 10.5 oz/yd (No. 8)	.62	.62	.00
QM1 Cotton Sheeting, Bleached 4 oz/yd	.66	.61	+.05
QM2 Cotton Sateen, Prepared for Dyeing, 9 oz/yd	.72	.68	+.04
QM3 Cotton Sateen, Olive Drab (06107) 9 oz/yd	.22	.20	+.02
QM4 Cotton Sateen, Undyed 9 oz/yd	.72	.69	+.03
QM5 Cotton Sateen, Light Grey 9 oz/yd	.60	.56	+.04
QM6 Cotton Sateen, Medium Grey 9 oz/yd	.53	.50	+.03
QM7 Cotton Sateen, Dark Grey 9 oz/yd	.24	.23	+.01
QM8 Cotton Sateen, Black 9 oz/yd	.14	.12	+.02
QM9 Cotton Sateen, Deep Black 9 oz/yd	.13	.08	+.05

transmit less energy in the visible than in the infrared, such as the *Golden Plate* and red glass, are lower than the measurements with the directional radiometer. Further, examination of the spectral data of the higher reflecting cloths shows that the spectral reflectance characteristically decreases in the near infrared. The reflectance values of these cloths measured with the solar integrating sphere are likewise higher than the integrated values.

The above performance suggests that the integrating sphere is slightly selective, the magnesium oxide coating having a higher reflectance in the visible than in the infrared. The transmittance measurement of the red glass filter provides a quantitative measure of the selectivity of the sphere. Spectral transmittance measurements of this filter disclosed that it had a sharp cutoff at 0.70 microns and transmitted at longer wavelengths only. Since the values measured by the two techniques differed by 20 per cent, the integrating sphere is about 20 per cent more efficient in the visible than in the infrared. This selectivity is thus no less than that which would be expected for a Coblentz sphere, but the selectivity of the Coblentz sphere lies in the most important region of the spectrum.

The comparisons of data in Tables I, II, and III indicate that the solar reflectance can be determined

within about ±0.04 for all materials but those whose special characteristics differ greatly from the visible to the near infrared. In the case of the latter materials, errors of about 20 per cent could occur.

Design

Primary design requirements were that the instrument should be inexpensive yet reasonably accurate. These considerations suggested the use of naturally-occurring sunlight for total measurements. The use of natural sunlight in turn requires the instrument and detection system to be portable and rugged.
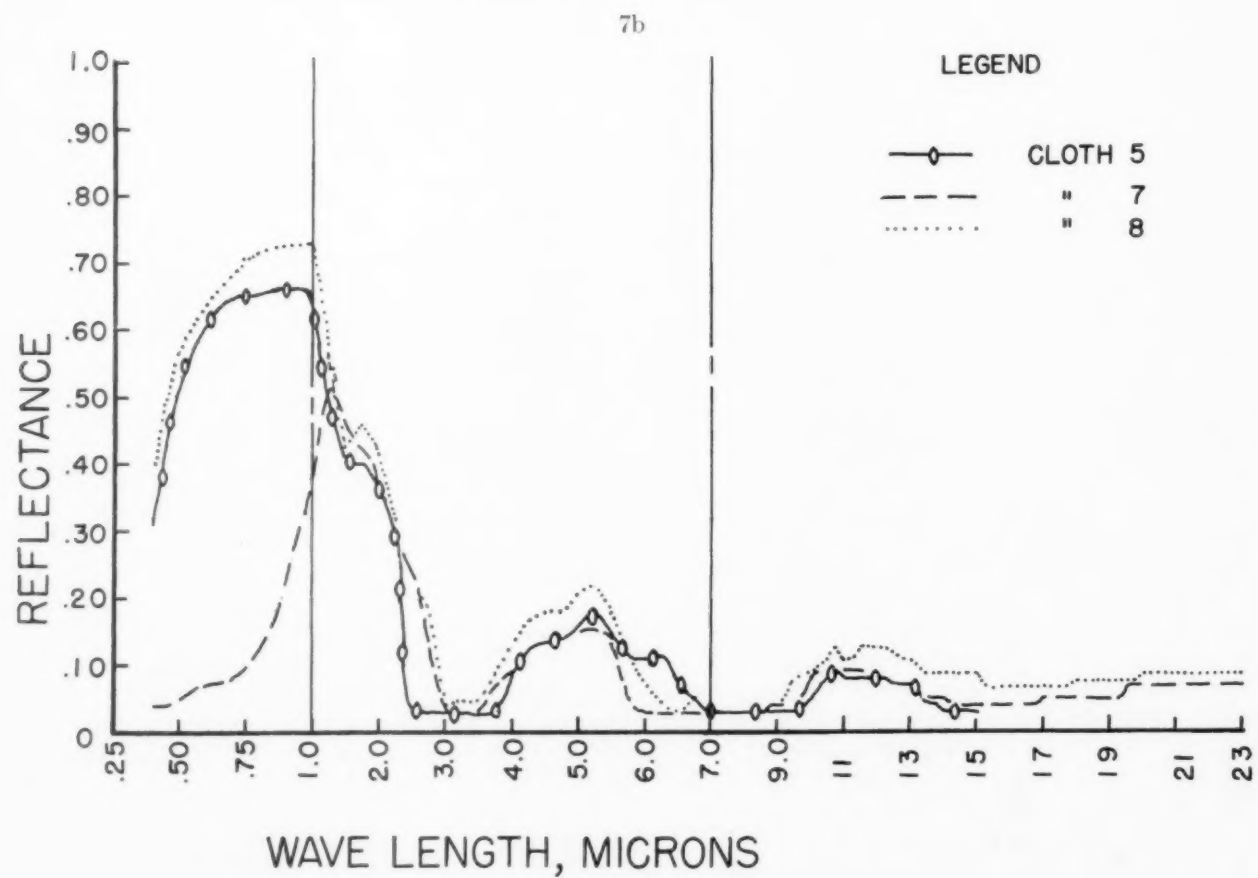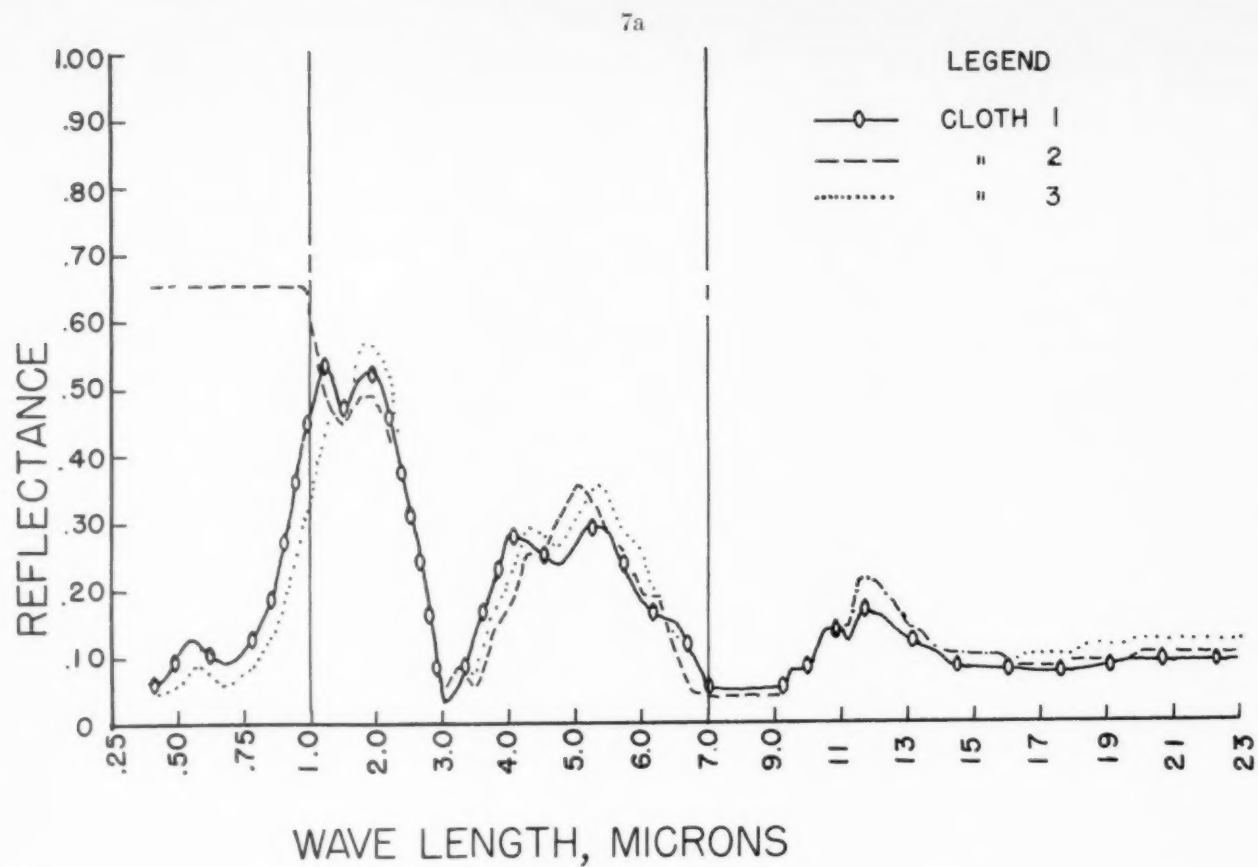
The key feature of the design was the use of a silver-plated constantan thermopile for the detector. This detector is inexpensive and rugged. At the same time it is a quite nonselective and diffuse detector which provides a signal sufficient to be measured with a Leeds and Northrup 8662 portable potentiometer or with a standard recording potentiometer.
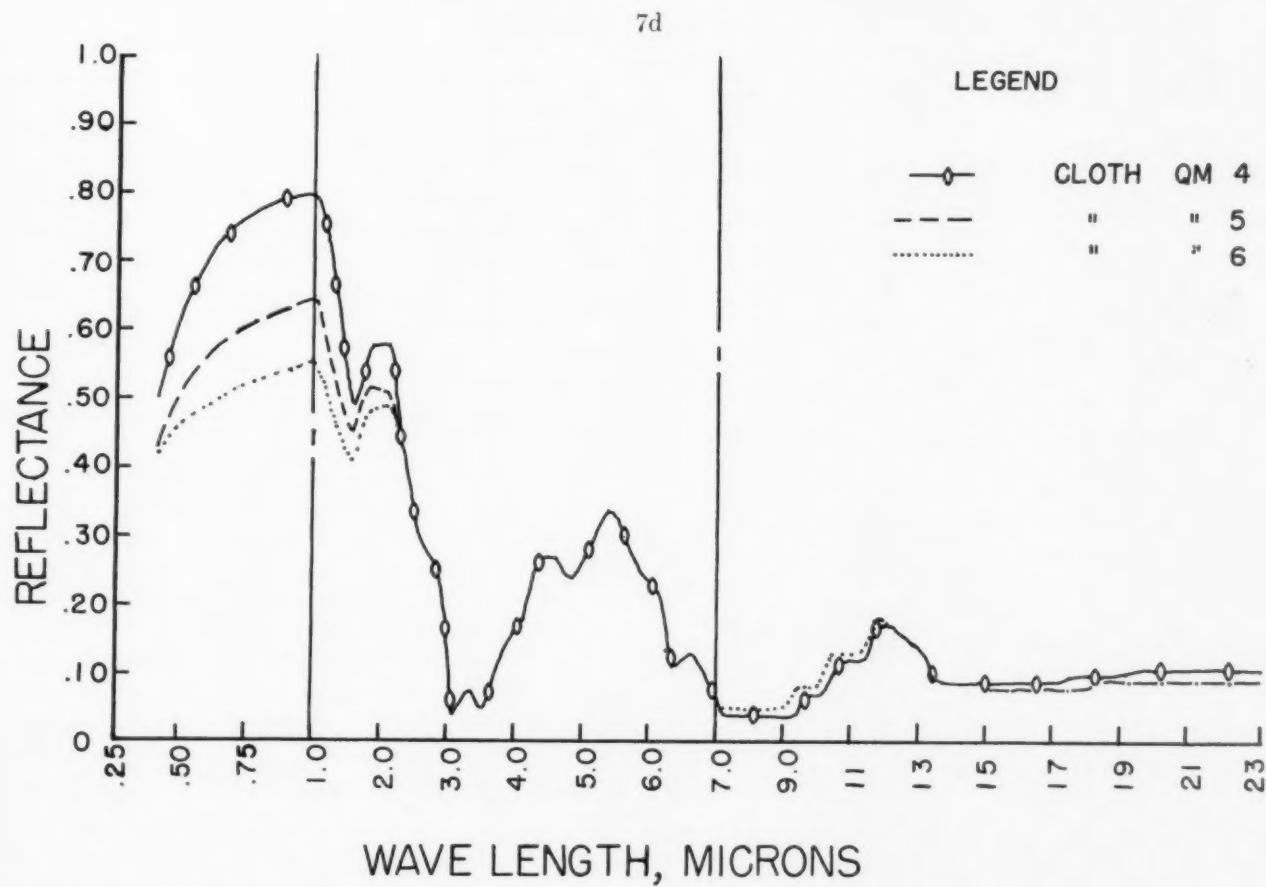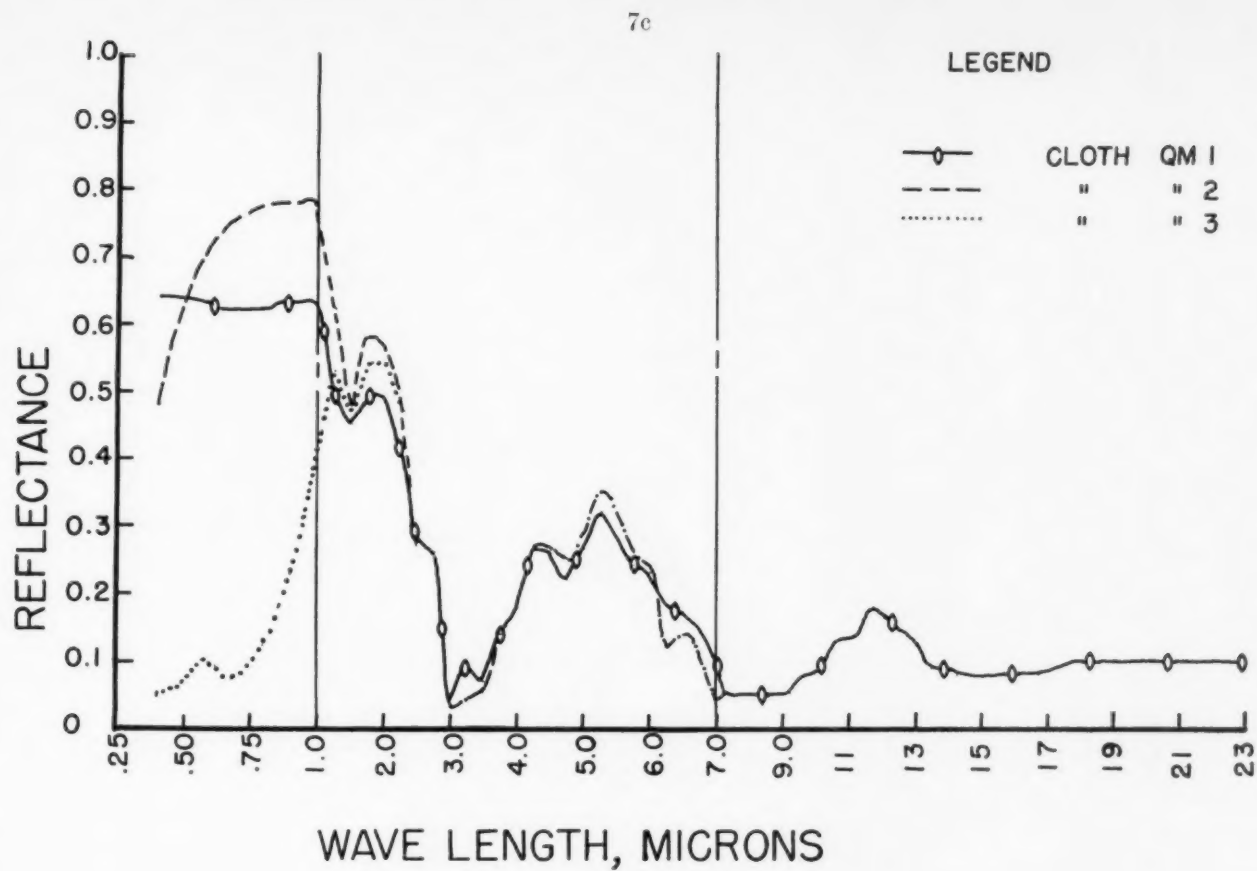
The requirements for the sphere coating in particular were that it be diffuse, as nonselective in the solar spectrum as possible, easy to apply and durable. For these reasons it was decided to apply magnesium oxide over a titanium dioxide paint so that diffuseness would be assured even if small segments of the magnesium oxide coating should flake off during handling of the instrument. It was also decided that simple smoking with burning magnesium would be much more convenient than smoking with a high voltage potential as recommended by Tellex and Waldron[15] although subsequent experience by the authors has shown that actually the reverse is true. Since simple smoking was employed, it was not feasible to build up a coating thickness much over 0.03 in. without running the risk of flaking while the instrument was transported.

As in the rest of the design, selection of the relative sizes of the sphere, detector, and various ports required trading some advantages for others. As shown by Jacquez and Kuppenheim[11], to obtain high sphere efficiency (high output signal for given energy input) the detector, if it is uniformly sensitive, should be large compared to the sphere, covering the entire sphere in the limit. Similarly, Jacquez and Kuppenheim show that there are optimum port-to-sphere-diameter ratios for maximum sphere efficiency.

High sphere efficiency is advantageous in two ways. First, if the output signal is quite large, band pass filters may be employed to obtain the coarse spectral characteristics as well as the total solar reflectances of the material tested. Second, the larger the relative size of the detectors and ports the less selective is the sphere, since there are fewer interreflections.

However, sphere efficiency is not the sole design criterion. It is difficult to make a large uniformly-

7a

LEGEND

	CLOTH 1
	" 2
	" 3

WAVE LENGTH, MICRONS

7b

LEGEND

	CLOTH 5
	" 7
	" 8

WAVE LENGTH, MICRONS

7c

REFLECTANCE

WAVE LENGTH, MICRONS

LEGEND

CLOTH QM 1
"   " 2
"   " 3

7d

REFLECTANCE

WAVE LENGTH, MICRONS

LEGEND

CLOTH QM 4
"   " 5
"   " 6

LEGEND

—◇—	CLOTH	QM	7
— — —	"	"	8
··········	"	"	9

(y-axis) REFLECTANCE: .0 .90 .80 .70 .60 .50 .40 .30 .20 .10 0

(x-axis) .25 .50 .75 1.0 2.0 3.0 4.0 5.0 6.0 7.0 9.0 11 13 15 17 19 21 23

WAVE LENGTH, MICRONS
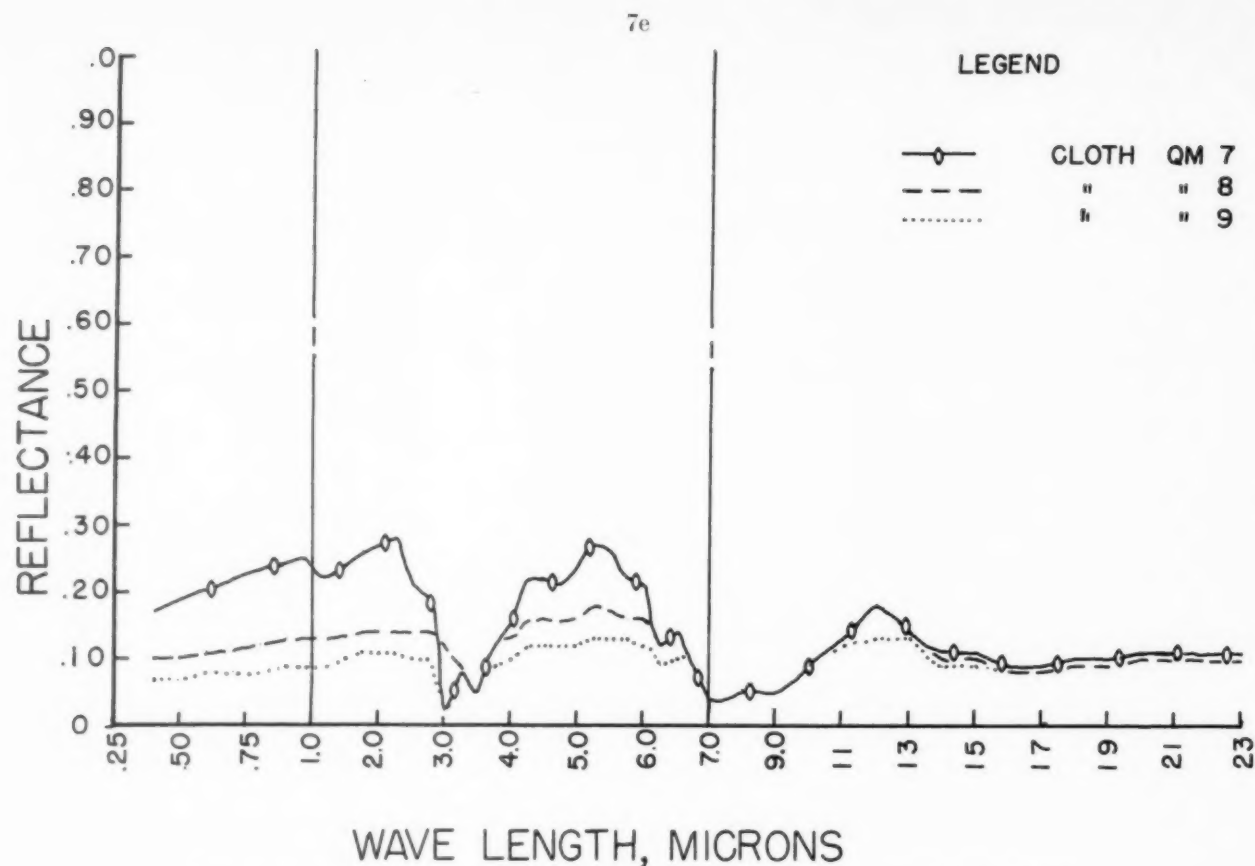
FIGS. 7a–7e—Spectral Reflectances of Various Cloths (See Table II for sample descriptions)

TABLE III—Comparison of Transmittances of Glasses
Obtained from Solar Reflectance Integrating Sphere
and Directional Radiometer

Glass Sample	Solar Reflectivity Meter	Directional Radiometer	Discrepancy
Golden Plate (amber glass)	.76	.82	− .06
Mirror Pane (half-silvered glass)	.08	.11	− .03
Color Clear Plate (plate glass)	.92	.94	− .02
1½ Plexiglass	.85	.83	+ .02
1¼ Plexiglass	.88	.86	+ .02
E.Z. Eye Glass (blue tinted glass)	.56	.51	+ .05
Heat Absorbing Glass (blue tinted glass)	.56	.52	+ .04
Red glass (short-wave cut-off at 0.7 μ)	.36	.44	− .08

sensitive spherical detector, and errors due to sample specularity must be considered. Further it is undesirable to test a quite small sample, since radiation characteristics may vary locally while a statistical mean is desired in technological applications.

Errors due to sample specularity arise from two sources[3, 11]. In the case of reflectance tests, too large (or, conceivably, too small) a fraction of the energy first reflected from the sample may escape out the entrance port. Similarly in reflectance and transmittance tests, too large or too small a fraction of

energy from the sample may strike the detector before being diffused by the sphere.

An example of the first problem is the use of a normal angle of incidence. In the case of perfectly diffuse materials compared to a perfectly diffuse reference, no error is involved. But in the case of a perfectly specular material, the energy is reflected back out the entrance port. Use of a slight off-normal angle of incidence removes the difficulty for the perfectly specular material, but not all materials are perfectly diffuse or perfectly specular.[6] For these partially-diffuse materials considerable error may occur unless the entrance port is small compared to the sphere.

Similarly, an example of the second problem due to sample specularity is the case of a detector location such that all incident energy reflected by a specular sample strikes the detector. If a specular material is compared to a diffuse reference in such a sphere, a completely erroneous result is obtained. Relocation of the detector away from the pencil of specularly reflected rays remedies the problem only for the perfectly specular example compared to a perfectly specular reference.

The second problem can be avoided by masking the

entrance port and sample ports from the detector. Such masking is practical only when the ports and/or detector are small compared to the sphere. Otherwise the masks must be so large as to introduce other sources of error.

It is seen that these considerations lead to conflicting design criteria. As a result it was decided to sacrifice sphere efficiency somewhat. A sample area of about one square inch was selected along with a convenient thermopile size The entrance port, which had to be the size of the illuminated sample area, was made small compared to the sphere by making the sphere large. Further, for simplicity no masks were used. However, errors due to specularity were somewhat minimized by locating the detector close to the sample ports so that energy reflected from the sample directly to the detector occurred at angles of about 75° from the normal. If anisotropies of a sample surface indicate the possibility of significant energy being reflected directly to the detector, error can then be reduced by repeating tests with various azimuthal angles of incidence. Specularity errors due to lack of energy reflected directly to the detector could be about $(1 - \rho)$ or about 6 per cent.

Improvement

The area of major improvement lies in using a less selective sphere coating or possibly using a selective thermopile detector receiver strip which compensates for the selectivity of the sphere wall. The spectral reflectances of magnesium oxide reported in the literature[5, 12, 14, 15] indicate a possible method of improvement.

For the sphere with small detector and ports, the spectral efficiency is proportional to $\rho_\lambda/(1 - \rho_\lambda)$. Since ρ_λ is fairly close to one, it is the variation of $1 - \rho_\lambda$ with λ which causes the greatest variation in the efficiency. If the slope of ρ_λ with λ is fairly insensitive to the coating thickness, as seems to be illustrated in the measurements of Middleton and Sanders[12], then the fractional variation of $1 - \rho_\lambda$ decreases as the general level of ρ_λ decreases with decreasing coating thickness. Deposit of a thin layer of magnesium oxide over a polished metal which has the opposite spectral behavior may then yield a relatively flat efficiency in the important region of 0.35 to about 1.8 or 2 microns. The coating cannot be so thin as to be partially specular, or errors due to sample specularity will be increased. Further, sphere efficiency is sacrificed by use of thin wall coatings.

Possibility of further improvement is offered by installation of masks as discussed previously. Minor improvements would consist of a vibration-free mount, a heavier gage thermopile housing wall, and more insulation, since vibration and zero drift occur in high winds.

SUMMARY AND CONCLUSIONS

The described integrating sphere makes possible the determination of the total reflectance of materials irradiated by actual solar energy with an uncertainty of ±0.04 determined from comparisons with integrated spectral values. Since the sphere is slightly selective, weighting the visible portion of the spectrum about 20 per cent more than the near infrared portion, greater errors may occur for samples which are highly selective in the solar spectrum.

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Methodology for Determination of Performance Characteristics of Spectrally Selective Absorbers

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This is a thought provoking paper centered about a theoretical technique for designing solar devices which use spectrally selective surfaces. A thermoelectric converter for use in space vehicles and using a parabolic cylinder reflector is treated in some detail. The use of such units in space brings us into an era of "no-costs-barred" design of such devices. The need for curves giving absorptivity, reflectivity, and transmissivity versus wavelength for the range 2×10^{-7} to 2×10^{-5} meters is pointed out. The inadequacy of lumped parameters (total absorptivity, total emissivity, etc) in work involving spectrally selective surfaces is discussed. A modern system of units (meters, joules, kilograms, etc) is proposed. Need is pointed out for research to determine the effect of microgeometry of surfaces on their radiation properties. A further need for study of the design of minimum mass fins for discharging heat by radiation is indicated.

INTRODUCTION

Systems for converting solar energy into electrical power are today being built for use in space vehicles. Thus the emphasis has shifted from low cost solar operated devices for use by the most backward and very poorest people of the earth, to "cost-is-no-problem" devices to be used in the most advanced scientific equipment of our age. This new application opens many doors. Very expensive materials and techniques may now be used. Sophisticated orientation devices and elaborate control systems may be employed. However, the two fields of application (which are now so widely divergent) may move toward each other—as the standards of living of our more backward peoples rise, and the methods and materials of the new technology become more widely known.

Fig. 1 shows a typical solar converter currently being considered for use with space vehicles. The parabolic mirror serves to focus incoming solar radi-

ation on the underside (the hot surface) of the thermoelectric generator. In passing upward through the generator, a portion of the heat is converted to electrical energy. The waste heat arriving at the upper surface (the cold surface) is delivered to the fin and from thence is radiated to space. The sun shield prevents incoming solar radiation from striking either the surface of the fin or the upper surface of the generator (both of which should be kept as cool as possible).

DEFINITION OF PROBLEM

The solar converter should be designed to maximize the ratio of electrical power output to total mass of the system. This is in marked contrast to conventional power generating systems (such as the automobile engine) in which the ratio of output power to input power is maximized. Cost is the determining factor. For the auto engine, cost of the gasoline is high relative to initial cost of the engine. Hence, a high ratio of power output to gasoline consumption (efficiency) is desired. For the solar converter, cost of placing the system in orbit is some $20,000 per kg—while the sunshine is free. Hence, a high ratio of power output to total mass is desired.

Other items (such as stored volume, ability to withstand the stresses of launch, durability in space, orientation requirements, etc.) are important—but do not serve as well as a basis for design as does the power-to-mass ratio.

ANALYSIS

Fig. 2, a cross-sectional view of the converter proper, shows thermal items of interest.

Performance of the system will be a function of the following:

(1) The ability of the mirror to concentrate solar energy upon the underside of the generator.

(2) The ability of the underside of the generator to absorb the incident solar radiation (while reradiating very little).

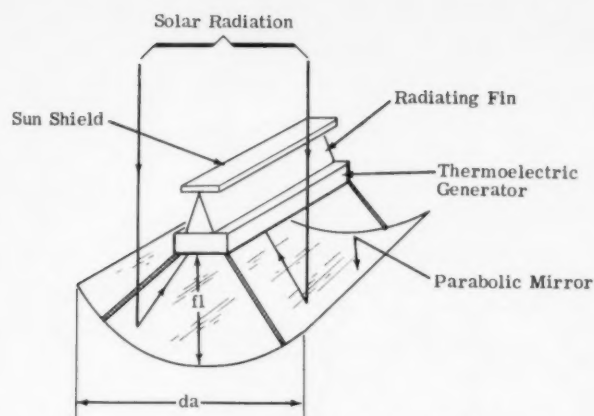(3) The ability of the fin to radiate waste heat very

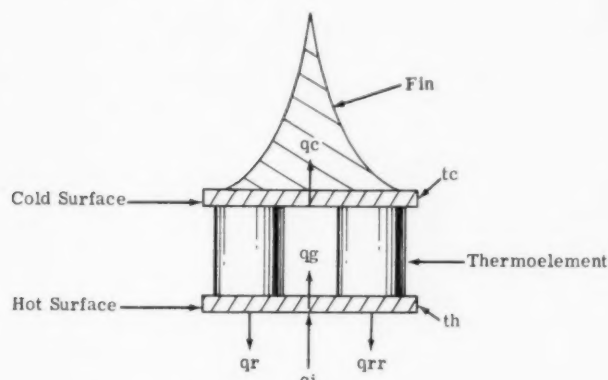Fig. 1—Typical Device Operated by Solar Energy

Fig. 2—Analysis Diagram

efficiently and thereby maintain a low temperature at the cold surface.

(4) The efficiency of the thermoelements in converting heat to electricity.

The pertinent terms, equations, and procedures may be arranged in a systematic manner to facilitate computation (either by hand or by a digital computer). Discussion of each term will follow the presentation of terms and equations.

(1) dqss—Spectral distribution of solar energy at earth's distance from the sun (see discussion after step 19).

(2) dm—A delivery function for the mirror defining the distribution of radiant energy on the hot surface of the converter.

(3) sph—Spectral characteristics of hot surface.

(4) spf—Spectral characteristics of fin.

(5) gef—Geometric factor for fin.

(6) eff—w/deg—Ratio of electrical power out to difference in temperature across elements.

(7) th—deg—Temperature of hot surface.

(8) tc—deg—Temperature of cold surface.

(9) dqi = f (dqss, dm)—Spectral distribution of flux arriving at hot surface.

(10) dqr = f (dqi, sph)—Spectral Distribution of flux reflected at hot surface.

(11) qrr = f(th, sph)—w/m²—Radiant flux radiated from hot surface. (Dimensions of the term are "watts per meter squared"). It is suggested that the present time (when solar converters are coming to be used in space activities) is most appropriate for adopting a "more modern" system of units. The meter is proposed as a universal unit of length—whether one is measuring wavelengths of light, or the distance to the farthest star. The joule is proposed as the universal unit of work—whether one is measuring the heat required to raise the temperature of water or the energy contained in cosmic radiation.)

(12) qh = qi − qr − qrr—w/m²—Heat flux delivered to generator.

(13) pe = eff (th − tc) qh—w/m²—Electrical power delivered by generator.

(14) qc = qh − pe = f (tc, gef, spf)—w/m²—Heat flux arriving at cold surface.

(15) Study the results of 14 and adjust tc until the equation is satisfied.

(16) kc = f (th, tc, qh)—w/m² deg—Thermal conductance of generator.

(17) ms—kg—System mass. Obtained by summing the masses of the several components.

(18) fmt = pe/ms—w/kg—Figure of merit. Ratio of power output to mass of system.

(19) Repeat the above for a number of different configurations, selecting as best that system which has the highest figure of merit.

Item 1—dqss, is best considered in the form of a curve—as shown in Fig. 3. The term "dqss" is read "—the derivative with respect to wavelength of the radiant power falling on one square meter of surface area exposed normally to solar radiation". The area under the curve gives the intensity of the incident radiation (qss) in watts per square meter. The value of 1400 w/m² is an often quoted figure for qss above the atmosphere. At the surface of the earth the value varies with weather, latitude, time of day, and season. A value of 700 w/m² is often quoted. The shape of the curve approximates that of a black body. However, the approximation is not sufficiently close to warrant the use of a 6000°K black body curve in place of the solar curve—except for the roughest of calculations.

Item 2, dm, is given in Fig. 4 (for a typical mirror).

The shape of the curve varies with the aperture ratio of the mirror (da/fl in Fig. 1). The peaked nature of the curve is primarily due to the fact that the sun is a round body. Items which have a lesser effect upon the shape of the curve are:

1. The variation of intensity with radius in the solar disc.

1.8 ⑨

1.6 ⑨

1.4 ⑨

1.2 ⑨

dqss

w/m³

⑨

8 ⑧

6 ⑧

4 ⑧

2 ⑧

0   0.2   0.4   0.6   0.8   1.0   1.2   1.4   1.6   1.8   2.0   2.2   2.4 ⑥ m
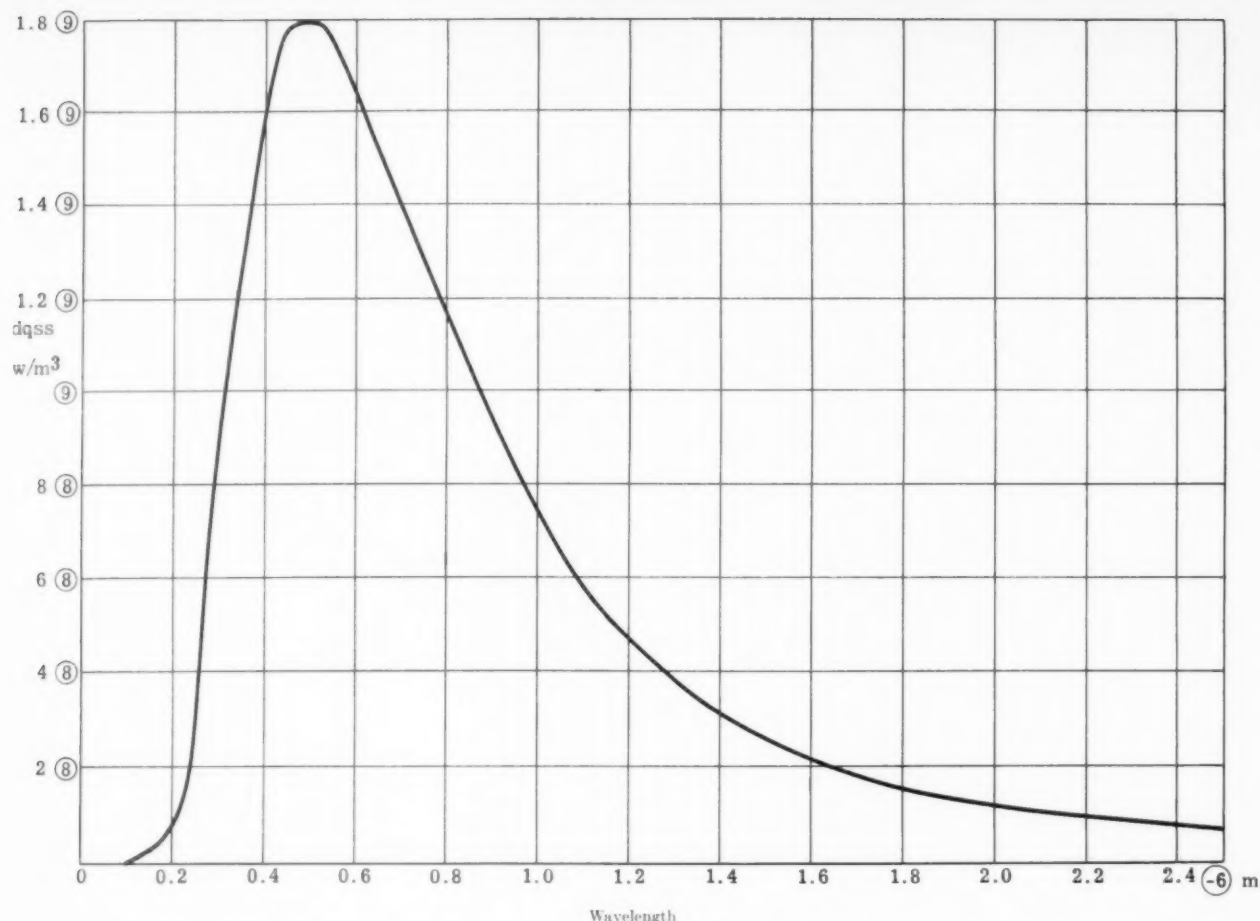
Wavelength

FIG. 3—Spectral Distribution of Solar Radiation

2. Variation of reflection characteristics of mirror with angle of incidence of incoming radiation.

3. Imperfections in the mirror surface.

Item 3, sph, is given in Figure 5 (for a typical surface which might be used in the current application). The curve gives the spectral absorptivity, reflectivity, and transmissivity for the surface throughout the wavelength region of interest—2 ⑦ m* to 2 ⑤ m. The shape of the curves will vary from material to material. The shape will also vary with angle of incidence of the incoming radiation—and may vary with the temperature of the surface. At the present time curves such as those given above just simply are not available—although programs are under way at several research institutes to obtain such curves.

Item 4, spf, is a similar curve for the fin. In general, a surface for the fin will be chosen to give a high value of emissivity in the range from ⑥ to 2 ⑤ m wavelength. This will cause the fin to act very efficiently as a radiator at the temperatures of interest $(300–500°K)$.

Intensity of Radiation
(w/m²)
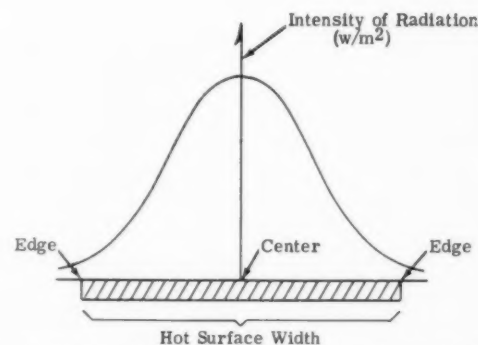
Edge   Center   Edge

Hot Surface Width

FIG. 4—Distribution of Radiation over Cross Section of Hot Surface.

The spectral characteristic of the cold surface is of opposite characteristic to that of the hot surface. The latter was selected to have a high absorptivity (and also emissivity) in the spectral region where solar energy is concentrated, and a low emissivity in the longer wavelength region where the surface itself would tend to radiate. The literature refers to such a surface as a "selective absorber".

The characteristics of such an ideal absorber may be

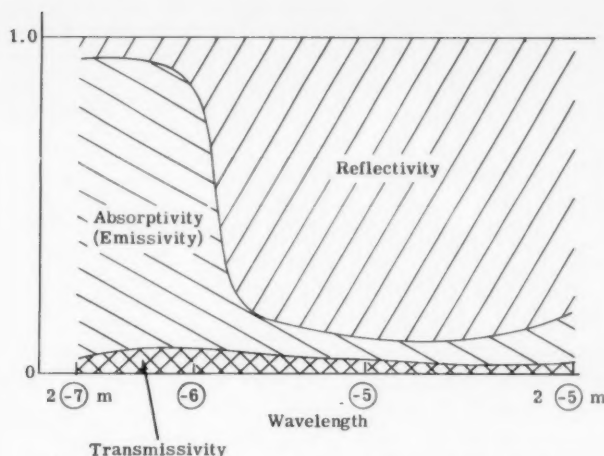* Shorthand for 2×10^{-7} meters.

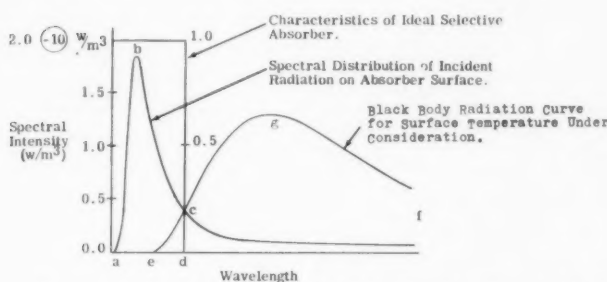FIG. 5—Spectral Characteristics of Typical Hot Surface

FIG. 6—Determination of Cut-Off Wavelength for Ideal Selective Absorber.

obtained from the graph of Fig. 6. An ideal selective surface has unity absorptivity below the wavelength indicated by point d, and unity reflectivity above. It will absorb heat flux represented by area abcda. It will radiate heat flux represented by area ecde. Net heat retained within the surface is represented by area abcea. This last area is greater than the corresponding area which would be obtained for any other selective surface. Consideration of Figs. 4 and 6 together reveals that the ideal selective surface is a function of:

(1) The spectral characteristics of solar energy—which determine the general shape of the incident curve of Fig. 6.

(2) The spectral characteristics of the mirror—which modify the shape of the curve by a small amount.

(3) The intensity distribution across the hot surface as determined from Fig. 4. This causes the amplitude of the incident curve of Fig. 6 to vary—which in turn shifts point c. It is noted that this intensity distribution will cause the characteristics of the ideal selective absorber to change as one proceeds from the center of the hot surface to the edge.

(4) The temperature of the hot surface—which affects both shape and amplitude of the black body curve of Fig. 6.

The ratio of area abcda to area abcfa is referred to as

the "absorptivity" of the surface. The ratio of area ecde to ecgfde is referred to as the "emissivity" of the surface. It is of interest to note that the ideal selective absorber is not that surface for which the ratio of absorptivity to emissivity is maximum. This ratio would be a maximum (infinite) for a surface having a cut-off wavelength corresponding to point e of Fig. 6. However, such a surface would be much less efficient in delivering heat to the generator than the surface with cut-off at point d.

Item 5, gef, is a geometric factor for the fin which coupled with spf determines how much heat the fin will radiate for a given cold surface temperature. It is possible that analytical study could reveal the proper relations. However, it is felt that experiment offers a more practical approach. Curves such as those of Fig. 7 could be obtained.

The curves of Fig. 7 would approximate 4th power curves. However, significant departures would result from two sources. First, radiation from the surface of the fin follows a fourth power law (assuming a gray body surface) while conduction through the fin follows a first power law. The result is that at low temperatures, the fin will tend to radiate as a whole; at high temperatures, the radiation will be largely restricted to the base region. Second, the surface will not be a gray body. As a result, the heat ejecting characteristics of the fin may change markedly with temperature.

Item 6, eff, is a function of the thermoelectric materials employed in the generator. It is generally about 6 per cent—quite low in value.

Item 7, th, is one of the so-called boundary values of the problem—it depends upon the past history of the hot surface. It is properly expressed as the integral of the net heat flux into the surface divided by the areal specific heat j/m² deg of the material. A temperature of 900°K for a generator using Lead Telluride (PbTe) elements is desirable.

Item 8, tc, is the second boundary value. For PbTe it should be 500°K or lower.

Item 9, dqi, is obtained for a particular point on the absorber surface by multiplying the dqss curve by the corresponding ordinate of the dm curve.
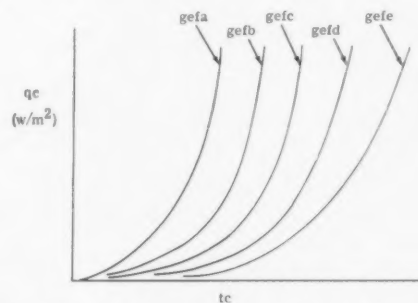

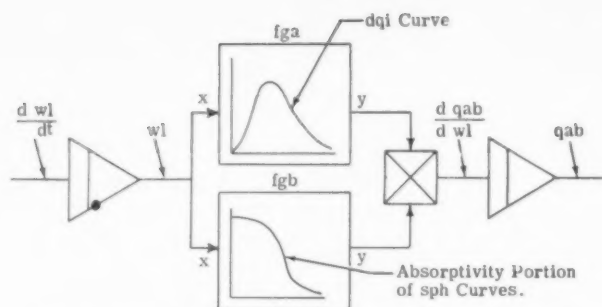FIG. 7—Curves Relating qc and tc for Various Fin Configurations.

FIG. 8—Analog Set-Up for Determining Action of Spectrally selective Surfaces.

Item 10, dqr, is obtained by multiplying point by point the ordinate under the dqi curve by the reflectivity ordinate of the sph curve and summing the area under the resultant curve.

Item 11, qrr, is obtained by multiplying point by point the ordinate under a black body curve corresponding to th by the emissivity ordinate of the sph curve, and summing the area under the resultant curve.

Item 13, pe, is to be maximized for the particular configuration under study. It would appear to require that th and qh rise and tc drop. Increasing the size (and consequent mass) of the fin causes tc to drop. On the hot surface the problem is more complicated. If th is raised, (referring to Fig. 6) qh must drop. The relationship is highly non-linear. Since tc is also a highly non-linear function of qh, the entire problem becomes most involved.

Item 14, qc, closes the problem. If the two equations are not satisfied, tc must be altered until they are.

For hand calculations, curves may be superimposed and multiplied by eye. A planimeter may then be used to obtain the area under the curves. A higher degree of accuracy may be obtained in handling the curves by using the analog set-up of Fig. 8.

Blocks fga and fgb may be function generators or curve followers. The system has been used and works quite satisfactorily. The problem may also be solved with a digital computer.

NECESSITY FOR USING SPECTRAL DISTRIBUTION CURVES

Heretofore radiant energy has been largely treated in terms of the quantity of radiation only. However, in the study of a system using radiant energy (such as the above discussed solar converter) the spectral distribution of that energy is fully as important as the magnitude.

Note that in the study of the thermoelectric generator, the spectral curve of radiation was used wherever the heat energy appeared as radiant energy. Only

when the heat was converted to sensible heat for passing through the generator was an integration carried out under the curve. Study will reveal that the problem can be solved in no other way.

Note further that no use was made of the "absorptivity" or "emissivity" of the surfaces involved. Instead, the spectral characteristic curves of the surfaces were used. Absorptivity varies with the spectral distribution of the incident energy. Emissivity varies with the temperature of the surface. But the spectral characteristics of the surface do not change with nature of incident energy and generally only slightly with temperature of the surface.

Also, nowhere in the study was mention made of the "temperature of the radiant energy (although the literature dealing with systems for concentrating solar energy are replete with references to the "temperatures" attained at their foci). The temperature of radiant energy becomes useful only in the study of black body cavities and their near equivalents. It is not useful in a study involving spectrally selective surfaces. The equilibrium temperature of an actual body placed at the focus of such a mirror is dependent upon:

(1) The spectra distribution of the incident radiant energy.

(2) The spectral characteristics of the surface.

(3) The geometry of the surface.

(4) The heat transfer properties of the body.

Thus, the temperature of such a body will not, in general, indicate the concentrating ability of the mirror. The items of interest in the study are:

(1) Spectral distribution.

(2) Direction.

(3) Polarization.*

NEEDED RESEARCH

The science of spectrally selective absorbers needs intensive work directed toward obtaining spectral characteristic curves such as that given in Fig. 5. Techniques must be developed for tailoring such surfaces to meet the requirements of specific applications. Variation of the characteristics with temperature, and with angle of the incident radiation must be studied.

While not mentioned in this report, the micro-geometry of the surface has a marked effect upon spectral characteristics. Such surfaces must be studied and the techniques of tailoring them to specific needs developed.

As indicated in the current paper, worthwhile study may be devoted to the design of minimum mass fins for transfering heat by radiation.

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* While not of interest in the current study, polarization plays an important role in the study of multiple reflections from mirrors placed at various angles relative to each other.

The techniques outlined in this paper need experimental verification (or invalidation).

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